TEXT-BOOKS OF SCIENCE

ADAPTED FOR THE USE OF

ISANS AND STUDENTS IN PUBLIC AND SCIENCE SCHOOLS

CHEMICAL PHILOSOPHY

INTRODUCTION TO THE STUDY
OF
HEMICAL PHILOSOPHY

THE PRINCIPLES
OF
THEORETICAL AND SYSTEMATIC CHEMISTRY

BY

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WITH ANSWERS TO PROBLEMS

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PREFACE

TO

THE TENTH EDITION.



It is now twenty-five years since the first publication of this little book, and in the history of a branch of science like Chemistry this is a long time. In the successive editions which have been called for, efforts have been made to introduce from time to time an account of such new discoveries or new theories as appeared likely to be useful to the student. The time has now come when new matter can no longer be incorporated into the old text. The influence of the new doctrines—especially those relating to stereo-chemistry, to electrolysis, and to the properties of solutions—is felt throughout every department of the science, and phraseology is necessarily so modified to suit the new points of view that no process of patching can be regarded as sufficient to bring old statements of fact or hypothesis into harmony with present ideas. Accordingly the book has been completely recast, and in large part re-written. Its general character as an elementary work has been

designedly retained, but it is believed that the student who has been sufficiently prepared by experimental practice in the personal observation of phenomena will find in it a fairly complete introduction to all the most important doctrines of modern chemistry.

ROYAL COLLEGE OF SCIENCE, LONDON:
October 1901.

EXTRACT FROM

PREFACE TO THE FIRST EDITION.

This little volume is primarily intended for the use of students. It aims at presenting a synopsis—brief indeed, and probably imperfect—of the leading principles of chemistry in such a form as to give the subject a more decided educational direction than has been hitherto customary.

In consideration of its peculiar fitness for developing the powers of observation, of reasoning, and of memory, no branch of experimental science deserves more emphatic recognition at the hands of educators than chemistry. In order, however, that its advantages may be reaped to the full I believe that the methods of teaching very generally prevalent in schools require to be considerably modified. I think teachers ought to realise the fact that chemistry, as a school subject, is not taught with a view to its practical applications to medicine, manufactures, or the arts, but because the study is calculated to quicken the faculties of observation, to strengthen the memory, and to engender a power and a habit of continuous thought, as well as to arouse new interests and open up new fields to the imagination. It is

of little consequence, in this view, whether or not the facts acquired can be turned to practical account; but it is of prime importance that the phenomena brought under their notice, and the manner in which those phenomena are presented, should be such as will compel the pupils to think.

Notwithstanding that the book does not profess to be a complete treatise on the subject, its contents will, I believe, be found sufficiently comprehensive to afford a tolerably general view of chemical theory as it exists at the present time. My desire has been to assist the student in attaining to broad and philosophic views of chemistry as a whole, and to accustom him to regard it as one out of many branches of physical science rather than as a mystery standing apart from other studies.

CLIFTON: *May* 1876.

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METRIC WEIGHTS AND MEASURES.

PREFIXES.—Myria-	10,000
Kilo-	1,000
Hecto-	100
Deka	10
( )	1
Deci-	$\frac{1}{10}$
Centi-	$\frac{1}{100}$
Milli-	$\frac{1}{1000}$

Inserting after the hyphen and in the brackets—
(1.) *Metre*, gives the measures of length.
(2.) *Litre*, ,, ,, capacity.
(3.) *Gram*, ,, ,, weight.

LENGTH.

1 METRE	= 10 decimetres.	(10 dcm.)
	= 100 centimetres.	(100 cm.)
	= 1,000 millimetres.	(1,000 mm.)
1,000 Metres	= 1 *Kilometre.*	

CAPACITY.

1 LITRE	= 1 cubic decimetre.	(1 c.dcm.)
	= 1,000 cubic centimetres.	(1,000 c.c.)

WEIGHT.

1 GRAM or the weight of 1 c.c. of pure water at 4° C.

	= 10 decigrams.	(10 dg.)
	= 100 centigrams.	(100 cg.)
	= 1,000 milligrams.	(1,000 mg.)
1,000 Grams	= 1 *Kilogram.*	

ENGLISH EQUIVALENTS.

	NEARLY	ACCURATELY
1 METRE	= 3 feet $3\frac{3}{8}$ inches or $39\frac{3}{8}$ inches.	= $39\cdot37_{079}$ inches.
1 KILOMETRE	= 1,100 yards	= $1093\ 63_{31}$ yards.
1 LITRE	= $1\frac{3}{4}$ Impl. pint or 35 ounces.	= $1\cdot76_{077414}$ pint.
1 GRAM	= $15\frac{1}{2}$ grains	= $15\cdot43_{23488}$ grains.
1 KILOGRAM	= $2\frac{1}{5}$ pounds	= $2\cdot20_{46215}$ pounds.

MEMORANDA.

Weight of 1 litre of hydrogen (at 0° C. and under 760 mm. bar. pressure) = ·0896 gram, or 1 crith.

Therefore 1 gram of hydrogen measures 11·16 litres.

For common purposes ·09 gram may be taken as the value of the crith. This corresponds to 11·1 as the measure of 1 gram.

Specific gravity of Hydrogen (Air = 1) = ·0693.
,, ,, ,, Air (H = 1) = 14·42.

$$5^\circ \text{ C.} = 9^\circ \text{ F.}$$

$$\therefore\ 1^\circ \text{ C.} = \tfrac{9}{5}{}^\circ \text{ F., and } 1^\circ \text{ F.} = \tfrac{5}{9}{}^\circ \text{ C.}$$

To convert C. into F. temperatures $\frac{C \times 9}{5} + 32 = F.$

To convert F. into C. temperatures $\frac{(F - 32)5}{9} = C.$

INTRODUCTION.

THE study of nature requires the employment of two distinct processes: the first is the observation or discovery of facts, and the second is the deduction of inferences from those facts. It is of the utmost importance to the student of chemistry to keep these processes apart from each other in his mind, and endeavour clearly to apprehend the proper functions of observation and experiment on the one hand and those of hypothesis and theory on the other. Chemistry is essentially an inductive science—that is, its theories are entirely based upon the results of observation and experiment; and although it is true that a theory once adopted is often sustained and strengthened by leading to the discovery of other facts, this is essentially a secondary process, and should always be so regarded. The assumption of theories based upon bad observations, or no observation at all, can be shown by the history of chemistry to have retarded the progress of knowledge very seriously in past times. The notion, for example, of an inflammatory principle called 'phlogiston,' and the general adoption of this idea during the greater part of the eighteenth century, for the purpose of explaining not only the process of burning, but other chemical changes, undoubtedly assisted in preventing the recognition of many facts which later became obvious, and in delaying the reception of the true theory of chemical change. An additional word of warning will not be out of place. A good theory is one which almost always leads to further discovery, but no theory, however justifiable,

can be regarded as final. Students are too apt to believe that an explanation having been once given, if it accounts for all known facts in a fairly satisfactory manner, will remain for ever established as representing the actual process or method of nature. All experience, however, leads to the conclusion that, however apparently complete a theory may be, an extension of knowledge will sooner or later lead to its being modified or absorbed into a more comprehensive theory, which will explain a wider range of phenomena. Theories in chemistry, therefore, as in other branches of physical science, can only be regarded as aids to the mind in apprehending and classifying the facts and things of nature, or, to use a familiar expression, they are only 'working hypotheses.' And when the word 'law' is used it must be understood only as a convenient abbreviated expression of coincidences which have been observed. The 'Law of Boyle,' for example, is only a synoptical statement of facts observed as to the behaviour of gases in regard to pressure, but no gas conforms strictly to the statement that its volume is inversely proportional to the pressure. A 'law of nature' is therefore not analogous to a legal enactment, which all are required to obey, and which admits of no variation. The science of chemistry is concerned with the composition of matter and with the study of the relations found to subsist between composition and properties. It is a science based, as already stated, upon the results of observation and experiment, and in the construction of theories the chemist makes constant use of the generalisations commonly referred to as laws of nature.

Among these generalised statements or laws two are of such fundamental importance that they are often regarded as axioms requiring no special notice or proof. The first of these statements affirms the *indestructibility of matter*. It is based upon the experimental results of a full century, for since the practice of using the balance was generally adopted, we have learnt that chemical changes are attended

by a redistribution of weight, but never by a destruction of substance. A thing burnt may disappear, but it is not destroyed, and in all cases the mass of a chemical compound is the sum of the united masses of its constituents. Conversely matter is never created by chemical processes, but is only changed in form.

The second of these two principles states that *energy is indestructible.* When two substances combine together to form a compound, the change is always attended by an absorption or evolution of heat. When, for example, hydrogen combines with oxygen, the production of the water is attended by a notable evolution of heat. This heat may be made to do mechanical work of some kind, such as the expansion of the gases and of the steam formed by their union, or if confined, it may produce pressure upon a piston or a gauge. Moreover, the amount of heat produced may be measured either by observing the amount of water the temperature of which may be raised by its means through a given number of degrees, or by the amount of ice which can be melted, or in other ways. And it is found that when thus measured, the quantity of heat produced is *constant for any given chemical change.* Heat was formerly supposed to be a kind of very fine matter having no weight, and it was referred to as one of the imponderable elements under the name of caloric. But it was proved by experiments made in the early part of the nineteenth century by Sir Humphry Davy and by Count Rumford, that if heat was matter, the quantity of it associated with ordinary matter was infinitely great, for heat could be continually produced in a mass of metal by continuous friction. Later, in 1843, the exact quantitative connection between heat and mechanical work was established by Dr. Joule, of Manchester, and thus heat was proved not to be matter but a mechanical condition of matter. Similarly, it is now known that heat, light, electricity, chemical action, and mechanical power are mutually convertible one into

another without loss, save that which can be accounted for in the imperfection of the material or of the apparatus used. A heated body, an isolated chemical element, and a mass of matter raised to a height agree in possessing the power of doing work of one kind or another, which, however, may be reduced to one form, and this power of doing work is called *energy*. Like matter, it can be neither created nor destroyed, and, though it may change in character, it is constant in amount.[1]

In order to facilitate the explanation of chemical and physical phenomena, it has been found convenient to revive, in a somewhat modified form, the ancient hypothesis that all bodies possessing extension and weight are made up of stuff, substance, or *matter*, which is not uniform and continuous throughout, but consists of separate very small portions. Each of these small masses, which are called *molecules*, is supposed to be to a certain extent independent of the rest and isolated from them. The hypothesis further requires us to suppose that the molecules constituting any given species of matter are all alike, in size, weight, and properties, and differ in these respects from other molecules. Thus the molecules contained in one drop of water are conceived to be precisely like the molecules in any other drop of the same liquid. Similarly the molecules in a given globule of the liquid metal mercury, or quicksilver, must be assumed to be like all other molecules of the same metal; but water molecules and mercury molecules differ altogether from each other in weight and chemical properties. It must be distinctly understood that molecules cannot be seen, and all the arguments upon which the assumption of their existence is founded are derived from the examination of masses of appreciable magnitude. We know nothing of isolated individual molecules; the examination of these

[1] For a complete exposition of the doctrine of energy the student should consult works on physics, especially Maxwell's *Theory of Heat*.

would be for obvious reasons impossible, and even if such a division were actually possible, the condition or properties of a single molecule would be in no way comparable with those of a mass of matter in which many molecules are imagined to be naturally aggregated by cohesion or otherwise. But we may assume that when one kind of matter affects chemically another kind, the smallest quantity of each which is capable of entering into the reaction consists of a determinate number of molecules. For the purposes contemplated in this book, then, a molecule may be defined as the unit of chemical action; that is, the smallest quantity which is able to take part in or result from a chemical change.

When two different kinds of matter are mixed together, chemical action often takes place between them. This action is supposed to be due to the union of molecules of the one kind with molecules of the other kind, or to an interchange of their components. The constituent parts of molecules [1] are called *atoms*.[2] Nothing is known concerning the true nature of atoms, though they have at different times been supposed to be hard particles of various geometrical forms, or vortices, like rings in air often produced from the top of a chimney, or from the funnel of a locomotive, and rendered visible by the smoke or steam. To the chemist the word simply means a small mass which cannot be divided, or, at least, has never been known to be divided, into smaller masses in the course of chemical action. An atom, then, is the smallest portion of matter which can be transferred from one molecule to another.

When the atoms within a molecule are all alike, the substance made up of such molecules is called an element. Most commonly, however, there are reasons for considering that the atoms composing a given molecule are dissimilar,

[1] Molecule, diminutive, from Lat. *moles*, a mass.

[2] Atom, from α, not, and τέμνω, I cut.

and then the body is a compound. The number of atoms in a molecule is very variable. A few elements have molecules which are assumed to consist of one atom only, others of two, three, or four; while in compound bodies the number may amount to hundreds.

Atoms are held together within the molecule, and probably molecules also are in certain cases united together by the operation of what is called, for want of a better term, *chemical affinity*, or *chemical attraction.* Of the nature of chemical attraction nothing is known. It cannot operate at a distance like gravitation, but requires that bodies should be in contact before they can combine together or act upon each other. It is apparently opposed by heat, for a sufficient elevation of temperature serves to break up the molecules of all compounds, and even those of many elementary substances, and in this disruption of molecular or atomic combinations by heat there is a very close analogy with the process of evaporation of a liquid. (*See* Dissociation.) It is closely related to electricity, and an electro-chemical theory, proposed by Davy in 1806, though never fully accepted, contains an element of probability which has led to its revival in a modified form in more recent times. This theory attributes chemical combination to the existence of charges of electricity of opposite kinds upon the atoms which unite, but there are several difficulties in the way which have never been satisfactorily cleared up, and are still a subject of debate. This question will be referred to again in a later chapter.

The study of those forces which affect entire molecules, and masses of molecules without regard to their composition, belongs to the domain of Physics. The immediate object of Chemistry is to ascertain the composition of bodies by the application of methods of *analysis* or of *synthesis*, but the science is not confined to the practice of these experimental arts. It has long been known that the same elements united in the same proportions do not necessarily

produce compounds having in every case the same properties—in other words, the order in which atoms are united together is not less important than their number, and *constitution* must be clearly distinguished from *composition*. (*See* Isomerism.)

The density, fusibility, volatility, colour, crystalline form, and other physical properties of both elementary and compound bodies are dependent upon the nature, number, and order of the atoms composing their molecules, and it seems to be now fully established that the chemical characters of an elementary atom are directly related to its mass, as represented by the value of its atomic weight. Furthermore, the combination and the separation of atoms or of molecules is attended by a distribution of energy, and every chemical change is attended by absorption or evolution of heat, and frequently by other physical phenomena.

The materials which compose the earth's crust, with its ocean and atmosphere and their inhabitants, may be roughly classified according to their mechanical condition into *solids* and *fluids*. Fluids are either liquids or gases.

A solid retains its form unless acted upon by pressure, by division with cutting instruments, by heat, or by solvents. Many solid bodies under suitable conditions assume definite geometric figures, which are generally bounded by plane faces, and thus give rise to crystals. This rigidity, by which the external form and relative position of parts is maintained, is due to what is called 'cohesion.' We should not, however, be justified in assuming that the constituent particles of solids are in a condition of absolute repose. Alteration of temperature and volume produced by the application of heat are attributable, according to the molecular theory, to the motion of the molecules, this motion being supposed to consist mainly in their rotation, or oscillation, or revolution, within a determinate space.

A liquid is recognised by its mobility, and by always assuming when at rest a horizontal level surface, except just

where it comes into contact with the vessel containing it. The several parts of a mass of liquid are not held together with the same amount of force that binds together the parts of a solid, for it is generally much less difficult to detach a drop from a mass of liquid than to break off a portion of a solid. The curved surface of a liquid at contact with a solid, the ascent of liquids in capillary tubes, and the spheroidal form of the rain-drop as well as of water sprinkled upon a greasy surface, are all effects of 'surface tension'—that is, these phenomena are due to the fact that the superficial layers of a liquid behave like an elastic membrane stretched over the liquid and exerting a pressure upon it. The volume of a liquid is scarcely affected appreciably by pressure, even when very great, and pressure communicated to any one part of a mass of liquid is transmitted almost instantly and without loss to every other part.

From the phenomena of liquid diffusion which will be alluded to further on, it seems probable that the molecules of liquids are constantly moving about. These motions, however, are sluggish in comparison with the corresponding intestine movement which is observed in gases, and this is, perhaps, to be explained by the assumption that the molecules of liquids are comparatively close together, so that their free motion is impeded by frequent collision.

Gases differ from solids and liquids in having practically no cohesion. A mass of gas exhibits no surface, like that of a liquid, and no gas can be confined in a vessel which does not enclose it on every side.

The bulk of a given portion of matter, solid, liquid, or gaseous, must depend both upon the temperature and the pressure to which it is submitted. The variation of volume produced in a solid or liquid by change of pressure or of temperature is very small when compared with the change produced by the same means in the volume of a gas. The law of the compressibility of gases was discovered by the Hon. Robert Boyle and published in 1662. It was ex-

amined independently and verified by Mariotte some years afterwards.

Law of Boyle.—'The volume of a given mass of any gas varies inversely as the pressure.'

Thus, if V is the volume when the pressure is P,
The volume of the gas becomes

$\frac{1}{2}$ V	when the pressure is . .	2 P
$\frac{1}{3}$ V	" " . .	3 P
$\frac{1}{4}$ V	" " . .	4 P
$\frac{1}{n}$ V	" " . .	n P
Also		
2 V	" " . .	$\frac{1}{2}$ P
3 V	" " . .	$\frac{1}{3}$ P
n V	" " . .	$\frac{1}{n}$ P

Hence the pressure which is produced by the *elastic force* or *tension* of a gas is proportional to its density.

So that if *pressure* increases,
density increases,
and *volume* diminishes.
Also, if *volume* increases,
pressure and *density* diminish.

Boyle's law is not absolutely obeyed by any known gas; but hydrogen and the other gases which are liquefiable with great difficulty conform to the law very nearly, and thus present the nearest approach to the condition of a perfect gas with which we are acquainted. With change of pressure the easily liquefiable gases and vapours increase or decrease in volume to a greater extent than more permanent gases.

It is usual to consider that the atmosphere possesses its average and normal density when, at the sea level and at the temperature of 0° C., the column of mercury in the barometer sustained by the atmospheric pressure is 760 millimetres (or 29·92 inches) high. This amount of pressure is often spoken of as one *atmosphere*.

In accordance with the law of Boyle the volume of a gas under altered barometric pressure can be calculated by the formula

$$\frac{V}{V_1} = \frac{P_1}{P},$$

in which V is the given volume under pressure P, and V_1 is the new volume when the pressure is altered to P_1. So that

$$V_1 = \frac{V}{P_1} \times P.$$

Example.—100 volumes of air are measured off when the barometric pressure is 740 mm.; what will be the volume of the same air when the barometer stands at 760 mm.?

$$\text{Here } V = 100,\ P = 740,\ P_1 = 760.$$

$$\text{Then } V_1 = \frac{100 \times 740}{760} = 97{\cdot}3 \text{ vols.}$$

Answer.

Solids, liquids, and gases alike expand upon the application of heat, but whereas each solid and liquid increases by a fraction of its volume which is peculiar to itself, all gases expand to practically the same extent by equal increment of temperature. In other words, whilst the coefficients of expansion of solids and liquids are all different, those of true gases are the same in every case.

Law of Gay-Lussac and Charles.—Air expands by $\frac{1}{273}$ of its volume at 0° for every increase in temperature of 1° C.

Thus	273 volumes of air at		. .	0
become	274	,,	,, . .	1
	275	,,	,, . .	2
	276	,,	,, . .	3
	273+t	,,	,, . .	t

Also, 273 volumes of air at			. . .	0°
become 272	,,	,,	. .	−1°
271	,,	,,	. .	−2°
270	,,	,,	. .	−3°
273 − t	,,	,,	. .	− t°

And generally 273 + t at t° become 273 + T at T°.

This fraction $\frac{1}{273}$, or ·003665, is called the coefficient of expansion, and represents almost exactly the increment or decrement which occurs in a measured volume of air or other permanent gas for every change of temperature of one degree centigrade, provided the pressure remains unchanged. The coefficient of all gases is *very nearly* coincident with that of air, and for chemical purposes may, without inconvenience, be assumed to be the same. Strictly speaking, however, every gas has a coefficient of its own, which, in the case of the more easily liquefiable gases, is perceptibly greater than the number given above, as may be seen by the following table :—

Coefficients of expansion for 1° C.

Air	·003665
Hydrogen	·003667
Carbonic oxide . . .	·003667
Nitrogen	·003668
Nitrous oxide . . .	·003676
Carbon dioxide . . .	·003688
Cyanogen	·003829
Sulphur dioxide . . .	·003845

It seems not unreasonable to suppose that such differences are due in part to the fact that in vapours and in the more easily liquefiable gases the influence of cohesion is not altogether annulled. It is conceivable that a vapour may consist of molecules which, unlike the independent molecules of perfect gases, may be connected together into com-

panies moving about much in the same way as individual molecules, but less rapidly.

Examples.—A certain mass of air measures 100 cubic centimetres at 0° ; to find its volume at 10°.

273 vols. of a gas at 0° become 273 + t vols. when the temp. is t° C.

In this case t = 10.

Then 273 c.c. at 0° become 283 c.c. at 10°,

$$1 \;\; ,, \;\; ,, \;\; \text{becomes } \frac{283}{273} \text{ c.c. at } 10°,$$

$$\text{and } 100 \;\; ,, \;\; ,, \;\; ,, \;\; \frac{283 \times 100}{273} \text{ c.c. at } 10°$$

Ans. 103·66 c.c.

Or, employing the decimal equivalent to $\frac{1}{273}$, let V_1 be the required volume and V the vol. given.

$$\begin{aligned} \text{Then } V_1 &= V\,(1 + \cdot 00366\, t) \\ &= 100\,(1 + \cdot 00366 \times 10), \\ &= 103\cdot 66 \textit{ Ans.} \end{aligned}$$

300 c.c. of air at 20° ; find the volume at 0°.

273 + 20 at 20° become 273 at 0°

$$1 \;\; ,, \;\; \text{becomes } \frac{273}{293} \text{ at } 0°.$$

$$\text{And } 300 \;\; ,, \;\; ,, \;\; \frac{273 \times 300}{293} \text{ at } 0°.$$

279·5 *Ans.*

Or, using the decimal coefficient, we say V_0, a certain volume of air at 0°, becomes 300 c.c. at 20°, or

$$V_0\,(1 + \cdot 00366 \times 20) = 300.$$

$$\text{Whence } V_0 = \frac{300}{1 + \cdot 00366 \times 20} = 279\cdot 5 \text{ c.c. } \textit{Ans.}$$

500 c.c. of air at 10° ; find the volume at −10°.

In this and all similar problems it is to be remembered that the coefficient of expansion is a fraction of the volume which the gas occupies at 0°, not at any other temperature.

273 + 10 c.c. of air at 10°
measure
273 − 10 c.c. at −10°.

Therefore 500 c.c. of air at 10°

measure $\frac{263 \times 500}{283}$, or 464·6 c.c. at −10°.

Or let V_{10}, V_0, and V_{-10} be the volumes at the temperatures 10°, 0°, and −10° respectively; then

$$V_{-10} = V_0(1 - \cdot 00366 \times 10) = \frac{V_{10}}{1 + \cdot 00366 \times 10} \times (1 - \cdot 00366 \times 10)$$
$$= 464 \cdot 6 \text{ c.c. } \textit{Ans.}$$

Air or any other permanent gas diminishes by $\frac{1}{273}$ of its volume for every degree of temperature travelling down the scale. If the same relations of volume to temperature were maintained, it is obvious that at −273° the volume would be *nil*, and the gas cease to exist. Such a temperature has, however, never been attained; and if ever such a degree of cold were reached, there can be no doubt that a gas exposed to it would liquefy, or that some change would occur whereby the gas would be released from obedience to the ordinary law.

Notwithstanding, however, that such a condition of things is practically beyond the reach of experiment, this consideration is important as furnishing the basis of an absolute scale of temperature. Calling −273° C. the zero point, we represent absolute temperatures by adding 273 to the number of degrees upon the ordinary Centigrade scale. From what has already been stated regarding the expansion of gases, it follows that, pressure being constant, the volume

of a mass of gas varies directly as the absolute temperature. This statement is sometimes referred to as the law of Charles, to whom we owe the discovery, towards the end of the eighteenth century, of the equal expansibility of the principal gases by heat.

Law of Avogadro.—All gases, when under conditions sufficiently remote from those which induce their liquefaction, are affected in the same manner and to the same extent by changes of pressure and of temperature. Differences of density, of chemical composition, or of chemical properties do not affect the generality of this statement. The volumes of heavy oxygen and light hydrogen, of simple nitrogen and compound marsh gas, increase and decrease according to the same law. It is impossible to avoid the inference from these facts that these gases, so different chemically, must be physically constituted alike. If now we admit the hypothesis that gases, like other bodies, are made up of small independent masses called molecules, and that heat causes these molecules to separate from one another, while cold or pressure causes them to approach, we are led to the assumption that in equal volumes of different gases at the same temperature and pressure there must exist the same number of molecules.

This statement, originally enunciated by an Italian physicist, Avogadro, in 1811, may now be regarded as a well-established truth.

But, like every other part of the molecular theory, this law owes its recognition by physicists and chemists, not to any direct proof that can be adduced from experimental sources in support of such hypothesis, but to the fact that nearly all observed chemical phenomena do not only harmonise with such views but find in them complete and satisfactory explanation.

Admitting the law of Avogadro, we see at once why gases are equally expanded by heat, why they are equally contracted by cold and pressure, and why they combine

together, according to the discovery of Gay-Lussac, in simple proportions by volume.

In a later chapter will be shown some of the consequences which follow upon an application of this law, and the important progress of chemical theory which has resulted from its adoption.

Graham's Law of Gaseous Diffusion.—A very remarkable property of gases and vapours is their power of mixing with one another, even in opposition to gravity.

If a bottle of any odorous gas is opened in any part of a room of constant temperature and free from draughts, the smell of the gas soon becomes perceptible in every part of the room, and, after the lapse of a short time, equally in every part. Notwithstanding that, as in the case of sulphuretted hydrogen, a heavy gas may be selected for the experiment, it would be easy to prove by analysis of the air that every part of it is equally impregnated with the foreign matter. Other experimental illustrations of the same law may easily be devised. A bottle of hydrogen held mouth downwards in the air for a short time soon becomes explosible. A jar of air inverted over another filled with carbon dioxide gas soon acquires the power of giving, like carbon dioxide, a precipitate with lime water. And this process of intermixture proceeds almost equally well if the gases are separated from each other by a partition formed of some porous material.

A thin plate of unglazed earthenware, a slice of artificially compressed graphite, or a cake of dry plaster of Paris, may be employed for the purpose. A very effective form of apparatus consists of a clay battery cell closed by a cork, through which a yard or so of glass tubing open at both ends is made to pass. By means of this simple apparatus it may be shown that different gases penetrate the porous clay with different degrees of rapidity, and that light gases effect a passage more quickly than heavier ones. The consequence of this difference of diffusion-rate is that a

difference of pressure is established inside the cell, and if the open end of the tube is dipped into water a certain quantity of gas is expelled in bubbles from below, or the liquid is forced by the atmospheric pressure up the tube. If, for example, the clay vessel previously full of air is surrounded by hydrogen gas, intermixture of the air within and the hydrogen without takes place through the clay; but since the hydrogen diffuses more rapidly than the air, the quantity of gas within is rapidly increased, and some of it visibly finds its escape from the open end of the tube through the water.

Early observations of and experiments upon gaseous diffusion were made by Priestley in the last century, and by Döbereiner in 1825; but Graham gave the explanation of the phenomena, and by precise and long-continued experiments established the law.

The velocities of diffusion of different gases are inversely proportional to the square roots of their densities.

Graham's experiments were for the most part conducted with a very simple apparatus, consisting of a straight wide glass tube closed at its upper extremity by a disc of porous stucco or graphite. This tube was filled with hydrogen or other gas over the mercurial trough, the graphite plate being covered during this operation with a sheet of guttapercha. The mercury within the tube was kept at the same level as the mercury in the trough, in order that there might be no alteration of pressure while the diffusion was proceeding and at the same time the temperature and barometric pressure were recorded. After the lapse of a certain interval, measured by a chronometer, the volume and composition of the residual gas could be determined.

The following table embodies some of the results obtained in this way, the pressure and temperature being supposed to be the same in all cases :—

Name of Gas	Density	Square Root of Density	$\frac{1}{\sqrt{\text{Density}}}$	Velocity of Diffusion
Air	1	1	1	1
Hydrogen .	·0693	·2632	3·7794	3·83
Marsh gas .	·554	·774	1·3375	1·344
Carbon monoxide	·9678	·9837	1·0165	1·0149
Nitrogen . .	·9713	·9856	1·0147	1·0143
Oxygen . .	1·1056	1·0515	·9510	·9487
Carbon dioxide .	1·529	1·2365	·8087	·812

It will be noticed that the observed rate of diffusion agrees very nearly with the rate calculated from the density of the gas; but in no case is there absolute concordance. This is, probably, in part due to the errors inevitable in any experimental investigation, especially where gases are concerned, but is also in some degree attributable to the fact that the diaphragm employed possesses an appreciable thickness, so that in passing through the pores the gas encounters considerable resistance.

By taking advantage of the unequal diffusibility of gases of different density, a partial separation of mixed gases may in some cases be effected.

The gases constituting atmospheric air, for example, may be, to some extent, separated from each other by causing a slow current of air to flow through a clay tube passing through a glass tube which has been exhausted as completely as possible by the air-pump. The nitrogen, being lighter and consequently more diffusible than the oxygen, passes more abundantly into the vacuous space, leaving the residual air richer in oxygen than it was originally.

The physical explanation of the phenomena of diffusion depends directly upon the mechanical theory of gases. The molecules of a gas are supposed to move constantly in

straight lines till they come nearly into contact with other moving molecules, or with the walls of the containing vessel. If these walls are perforated at intervals with apertures large enough to permit the passage of a molecule, we may conceive that although many molecules continue to rebound as though the surface were impervious, yet a great many others may find their way into and through these short passages, and so into the atmosphere beyond. Molecules from the external atmosphere may be assumed to pass inwards in precisely the same manner, and if the densities of the gases on the two sides of the partition are the same, the number of molecules passing inwards in a given time is exactly equal to the number passing outwards, and no change of volume or of pressure can result. But if the gases are of different densities, molecules of the lighter gas pass through more rapidly than those of the heavier, and a change is produced in the tension or elastic force of the gas enclosed in the porous vessel.

This pressure, exerted by a gas in opposition to that which it has to bear when enclosed in a vessel, is represented according to the kinetic theory as the result of the continuous showering down of its molecules upon the surfaces with which it is in contact. The molecules of different gases being of different masses, they must move with different degrees of velocity, the light molecules more rapidly than heavier ones, in order to produce the same amount of pressure. Hence, when the gas in contact with the porous surface is a light gas, its molecules must be supposed to fall upon a given area more frequently than when the gas employed is heavier, and consequently the opportunities for the escape of molecules through the pores are more frequent. Hence it is that light gases diffuse more rapidly than heavy gases.

Gases have not only the power of passing by diffusion through porous substances, but under certain circumstances penetrate membranes, and even sheets of metal which are

absolutely destitute of pores. This phenomenon differs entirely from diffusion, for it is not found that the lightest gases traverse such substances most rapidly; indeed, the contrary is more generally the case. Moreover, the metals which are so remarkable for their power of transmitting some gases are absolutely impermeable by others.

A few simple experiments will give the student an idea of the general character of the phenomena we are discussing. If a thin india-rubber balloon (such as are sold at the toy-shops), inflated with air, is immersed for a few minutes in a vessel full of carbon dioxide gas, the balloon becomes largely distended, and if a band of tape is fastened round it before the experiment, it generally bursts after immersion in the gas for a short time. A similar balloon filled with hydrogen or carbon dioxide gas quickly collapses when exposed to the air. Such a film of rubber appears to have no porosity, but rather to resemble a film of liquid in its relations to gases. The penetration of the rubber and similar colloids by a gas appears to be due to the absorption of the gas by one surface of the colloid and its transmission to the other surface by the agency of liquid and not gaseous diffusion. The liquefied gas then volatilises into the vacuum or atmosphere on the other side.

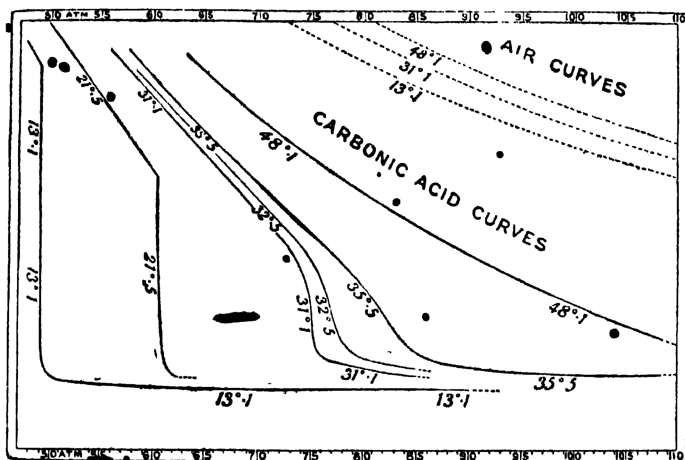
The passage of gases through metallic plates at a red heat was referred by Graham to a somewhat similar cause. Thus, at a red heat, both platinum and palladium, and even iron, are permeable by hydrogen gas; and this is evidently connected with the fact that the same metals are capable of absorbing and retaining considerable quantities of hydrogen when that element is presented to them under suitable conditions.

The compression of a vapour tends to produce the same change of state as lowering its temperature; that is, a portion is usually reduced to the liquid state. Considering the generally close resemblance between vapours and those bodies which are commonly called true gases, Faraday came

to the conclusion that the latter are not essentially different from the former, but are in truth the vapours of volatile liquids far removed at ordinary temperatures from their boiling points. This conclusion he verified experimentally by enclosing in strong Λ-shaped glass tubes materials capable of evolving the gases he wished to examine. On the application of a gentle heat to these materials gas was generated, and by its accumulation in the confined space sufficient pressure was exerted to cause its partial liquefaction. In this way ammonia, chlorine, and other gases were reduced to the condition of limpid liquids, and by the combined use of pressure and low temperature, produced by powerful freezing mixtures, a great many other bodies, which till then had been known only in the gaseous form, were also liquefied. Larger apparatus, constructed on the same principle as Faraday's glass tubes, were subsequently employed by different experimenters, and several gases, such as carbon dioxide and nitrous oxide, are liquefied on a large scale by compressing them by powerful force-pumps into steel cylindrical bottles fitted with stopcocks. By such methods all known gases were, with six exceptions, reduced to the liquid state.

Further advance, however, would have been impossible had it not been for an important discovery by the late Professor Thomas Andrews. His researches, published in 1869, disclosed the fact that if the temperature of a gas is above a certain *critical point*, which varies with the nature of the gas operated upon, liquefaction by pressure is no longer possible. The following diagram shows the effect of submitting air and carbon dioxide to pressure at different temperatures. When air or any similar gas, such as oxygen, hydrogen, or nitrogen, is submitted to gradually increasing pressure at any temperature near to that of the air a steady contraction is produced, and the pressure, p, multiplied by the volume, v, is practically constant, or $pv = 1$. When, however, a gas which is easily liquefiable is submitted to

pressure under the same conditions, it is found at all temperatures to contract at a much greater rate, and *pv* is less than 1. In the case of carbon dioxide the curves which show the effect at 13°·1 and at 21°·5 indicate by the sudden



change to the vertical that liquefaction begins at the pressures shown; while at temperatures above 31° or thereabout no amount of pressure that can be practically applied will bring about this effect. Andrews thus established a distinction between the state of gas above and below the critical temperatures. In the former state the substance is a *gas*, in the latter a *vapour*. This discovery gave the clue to the character of the six gases supposed to be permanent. Their critical points are at temperatures so low as to be attainable only by special arrangements and with great difficulty. Hence the failure of the earlier attempts to reduce these gases to the liquid state, notwithstanding the application of pressures represented by several thousand atmospheres.

Later experimenters applying the principle thus esta-

blished have employed liquid nitrous oxide and ethylene boiling under reduced pressure as cooling agents, and have succeeded in obtaining temperatures below the critical points of oxygen, nitrogen and air, and hence by the employment of comparatively moderate pressures it has become possible to liquefy these gases in considerable quantity. For a long time hydrogen alone resisted all efforts to reduce it to the liquid state, but by the employment of liquid oxygen, boiling *in vacuo*, a temperature of −211° C. has been reached, and when hydrogen, cooled to this temperature and under great pressure, is allowed to expand by relieving the pressure, a portion of the gas undergoes liquefaction and gives the appearance of ebullition within the tube containing it. The critical temperature of hydrogen is about −233°. The following table gives the physical constants of the six gases which, previously to 1877, were spoken of as 'permanent' gases, and of the gas argon discovered in atmospheric air in 1894.

Name	Critical Temperature	Critical Pressure	Boiling Point	Freezing Point	Freezing Pressure
	Below	Atmos.			mm.
Hydrogen (H_2) . . .	—	20·0	−252°·5	−257°	?
Nitrogen (N_2) . . .	−146·0	35·0	−194°·4	−214°·0	60
Carbonic oxide (CO) .	−139·5	35·5	−190·0	−207·0	100
Argon (A)	−121·0	50·6	−187·0	−189·6	?
Oxygen (O_2)	−118·8	50·8	−182·7	?	?
Nitric oxide (NO) . .	− 93·5	71·2	−153·6	−167·0	138
Methane (CH_4) . . .	− 81·8	54·9	−164·0	−185·8	80

The liquefaction of air, oxygen and hydrogen is now effected by the application of another principle. When a gas under pressure is allowed to escape from a small orifice against atmospheric pressure, or in other ways to do work, it becomes cooled, and the expanded gas thus cooled may be used to reduce the temperature of the gas while still under pressure. In this way a cumulative effect may be produced sufficient to bring about liquefaction of a portion

of the gas on its escape. Details of several forms of apparatus using this principle may now be found in several familiar text books.

The critical pressure is the pressure of the gas at the critical temperature when a very small increase of pressure or reduction of temperature causes liquefaction. In like manner the freezing pressure is the pressure of the substance when about to solidify. The liquids resulting from the condensation of these gases are all described as colourless with the exception of oxygen, which in the liquid state has a pale blue tint, and exhibits a remarkable absorption spectrum having several dark bands chiefly in the red, orange, and yellow.

The following table shows the amount of pressure in atmospheres necessary at the temperature of 0° to liquefy some of the more important of the gases :—

PRESSURE IN ATMOSPHERES—TEMP. 0° C.

Sulphur dioxide	1·53
Cyanogen	2·37
Hydrogen iodide	3·97
Ammonia	4·4
Chlorine	about 4
Hydrogen sulphide	10
Nitrous oxide	32
Carbon dioxide	38·5
Hydrogen chloride	about 42

Or they may be liquefied by cold alone under ordinary atmospheric pressure, as follows :—

Sulphur dioxide	condenses below	− 10°
Cyanogen	,,	− 22°
Ammonia	,,	− 36°
Chlorine	,,	− 50°
Carbon dioxide	,,	− 79°
Oxygen	,,	−183°
Air	,,	−190°

When a solid is transformed into a liquid, or a liquid into a gas, an apparently abrupt change of physical properties occurs, and heat is abundantly absorbed without producing elevation of temperature. But the transition from one state to another is by no means so sudden as appears from the consideration of cases like that of water. Many solids, such as iron, pass through an intermediate state, in which they are more or less plastic or viscid before they finally assume the liquid condition; and even the most perfect liquids with which we are acquainted are far from being absolutely mobile. Ether and alcohol, for example, flow more easily than water; but even these liquids exhibit a certain degree of viscosity.

Experiments commenced in 1822 by Caignard de la Tour, and continued and extended by Andrews, have shown that matter is capable of existing in a somewhat analogous condition intermediate between the liquid and gaseous states:—'By partially liquefying carbonic acid gas by pressure and then raising the temperature to 88° F., the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° F., no apparent liquefaction or separation into two distinct forms of matter could be effected, even when a pressure of three or four hundred atmospheres was applied.' (Andrews.) Nitrous oxide and sulphurous oxide, and other gases, give similar results. The striæ referred to are most probably the result of changes in density, caused by slight changes of temperature or pressure, as in ordinary liquids or gases when heated.

It thus appears that the various physical states of matter merge one into another by imperceptible gradations; and the molecular theory affords some explanation of this.

The change of a solid into a liquid, and of a liquid into a gas, is the result of alteration, generally increase, in the distances between the molecules and in the rapidity and character of their movements. The generally received opinion is something like the following. In a solid every molecule is attached to the surrounding molecules by cohesion, and it is free to move only about a certain mean position, which it never leaves so long as the body remains solid. In a liquid each molecule clings to its neighbours, but less firmly than in the solid, and it is free to move and does move about in the mass, though proceeding in any one direction a very small distance before its path is altered by encounter with other molecules. In a gas the molecules are independent of each other, and move with various degrees of velocity in straight lines. When two molecules approach each other the path of each molecule is altered. In the intermediate states of matter there is probably a mixture of these conditions. Thus, in a liquid at its 'critical point,' like carbonic acid gas at 88° F., some molecules are probably moving singly and independently, like the molecules of a gas, in the midst of masses of others which are closer together and moving more slowly, after the manner of molecules in a liquid, the relative proportion of molecules in these two conditions serving to determine whether the mass exhibits the character of a gas or a liquid.

Experiments by Crookes on the phenomena exhibited by highly attenuated gases led many years ago to the interesting discovery that when the tension of a gas is much reduced it possesses properties wholly different from those of the same gas under ordinary pressures. Under these circumstances, the number of molecules present in a given space being greatly diminished, the distance through which any one of them can move without collision is proportionately increased. When the pressure is reduced to about one-millionth of an atmosphere, and the discharge from an induction-coil is passed through the tube containing the

gaseous residue, no luminosity is observed in the contents of the tube, as occurs when the electric discharge is passed through an ordinary vacuum, but the molecules driven from the negative pole with great velocity traverse the whole space before them in straight lines, and striking upon the surface of the glass or upon other solid bodies placed in their path, cause them to emit a phosphorescent light. The stream of molecules flowing thus from the negative pole is also capable of moving light bodies suspended in its course, and when brought to a focus and allowed to impinge upon the surface of a solid it heats it strongly. These phenomena are exhibited equally well by hydrogen, carbon dioxide, or atmospheric air, and appear to have no connection with the chemical composition of the gas. It appears therefore that ordinary matter is capable of subsisting in a fourth state, differing as much from the solid, liquid, and gaseous states as these do from one another.

As a result of further investigations into the phenomena connected with the discharge of electricity through gases, it has been suggested that under certain circumstances the atoms of the gas may themselves be resolved into a comparatively large number of more minute particles, each carrying a charge of electricity. The subject is, however, still very obscure, and is not sufficiently developed to be suitable for presentation in an elementary book.

SECTION I.

CHEMICAL COMBINATION AND CHEMICAL COMPOUNDS.

CHAPTER I.

ELEMENTS, COMPOUNDS, AND MIXTURES.

WHEN water is exposed to a very high temperature or made the vehicle of an electric current, it disappears and is replaced by an equal weight of a mixture of two gases, hydrogen and oxygen. These two gases will, under certain conditions, again give rise to water and to exactly the same amount of water as at first.

Water then is said to be composed of oxygen and hydrogen. It is worth noting, however, that, strictly speaking, this can only mean that in proportion as the water is destroyed or ceases to exist, the gases make their appearance, and *vice versâ*, for in water we have no resemblance to hydrogen or oxygen, neither can we detect either of those bodies in water except by this process of so-called *decomposition*.[1]

Now, if the hydrogen thus obtained from water is sub-

[1] 'Cavendish and Watt both discovered the composition of water. Cavendish established the facts; Watt, the idea. Cavendish says, "From inflammable air and dephlogisticated air water is produced." Watt says, "Water consists or is composed of inflammable air and dephlogisticated air." Between these forms of expression there is a wide distinction.'—*Liebig's Letters on Chemistry*, p. 58.

mitted to a repetition of the same kind of treatment or to any other that may suggest itself, it refuses utterly to yield up anything that is not hydrogen. In other words, it cannot be decomposed. We find then that certain bodies,[1] such as water, may be resolved into two or more different kinds of matter, and these are called *compounds* ; while others like hydrogen cannot be split up in this manner by any means with which we are at present acquainted, and are regarded as *elements*.

It must be understood that the word 'element' is only provisional, and is merely intended to imply that in the present state of knowledge the bodies so called have resisted all attempts to decompose them.

Concerning the primal elements of nature nothing whatever is known. Some speculations concerning the constitution of the chemical 'elements' will be referred to later on, but it will be sufficient in this place to indicate the general nature of the investigations that have been made in regard to one or two of them.

Chlorine was discovered in 1774 by Scheele, who, in the language of the then prevalent theory, called it 'dephlogisticated muriatic acid.' This was equivalent to saying that it was muriatic acid deprived of its inflammable principle, hydrogen. After the discovery of the fact that many of the common acids contain oxygen, Berthollet, acting under the belief that it contained oxygen, gave it the name 'oxymuriatic acid.' Davy proved, in 1810, that it contained neither hydrogen nor oxygen, and gave it the name by which it has since been known and ranked with the rest of the elements.

Davy's chief experiments were as follows :—

The dry gas mixed with dry hydrogen unites with it without contraction and without the production of any water. Charcoal, previously freed from hydrogen and moisture, undergoes no change when intensely ignited in the dry gas

[1] It must be understood that bodies of definite characters, and not mere mixtures, are here referred to. (See pp. 35 to 42.)

by the voltaic current even for several hours, and no oxide of carbon is formed. Potassium, sodium, tin, copper, and other metals when heated in it combine with the whole of the gas, leaving no gaseous residue and forming no oxide of the metal. Phosphorus and sulphur, both highly oxidisable substances, unite with chlorine, but set free from it no muriatic acid. Chlorine mixed with dry ammonia produces only nitrogen and dry sal-ammoniac, and no water is formed. Electric sparks passed for a long time through chlorine gas produce no change in it. When chlorine acts upon a heated metallic oxide the amount of oxygen expelled is equal to that which is contained in the oxide and no more. So much for direct experimental evidence. The discovery of iodine, in 1811, and of bromine, in 1826, confirmed the position of chlorine among the elements, for if oxygen be a constituent of one of these bodies it must be present in them all. Further knowledge since obtained, the accurate determination of their atomic weights and the place they occupy in the system of classification which is based upon the numerical values of the atomic weights, establishes the claim of these three substances to be regarded as a natural group of elements. (See Halogens, Section II.)

The case of the fixed alkalies, potash and soda, is the converse of that of chlorine. Originally supposed to be elementary in consequence of the failure of all attempts to extract from either of them more than one form of matter, they had been suspected by Lavoisier to contain nitrogen, probably by reason of a certain resemblance to the volatile alkali ammonia, which was known to contain both hydrogen and nitrogen. By some of the same school it had been guessed that the alkalies and alkaline earths were compounds of metals with oxygen, in consequence of the resemblance which some of them, such as lime, present to oxides, like litharge, the composition of which was known. In 1807 it was known that the voltaic current would decompose acidified water into oxygen and hydrogen, and

that solutions of various salts were resolved into acid, which collected at the positive pole, and alkali, which always passed to the negative, also that many of the metals and their oxides might be separated from their compounds by the same agency. With these facts in view Davy exposed caustic potash to the action of a powerful electric current and obtained oxygen and potassium. Caustic soda was by the same means shown to contain sodium. These new metals were at first supposed to be compounds of hydrogen with potash and soda respectively, but in that case they ought, when burnt in oxygen, to produce the hydroxides. That this is not the case was shown by Davy.

As to potassium and sodium their elemental nature seems almost above suspicion, for there is no class of substances possessing so many characters in common as the metals, and if it could be shown that any one of them contained, for example, hydrogen, the same constituent might be expected to occur in all. The results of spectroscopic analysis, moreover, seem to place this question beyond doubt, for the spectrum of each metal is independent and shows no sign of containing an element in common with any of the others.

Other examples might be mentioned of substances long regarded as chemical elements ultimately showing their true character as compounds under the influence of some new agent or some improved mode of operating; thus, the substance regarded as metallic vanadium by Berzelius turned out to be an oxide of vanadium when examined long afterwards by Roscoe.

In the case of oxygen it is found that, by the action of electricity and otherwise, it may be converted into another gas, ozone, possessing remarkable characters quite distinct from those of oxygen. Nevertheless, oxygen ranks as an element because it yields in this way only one new body at a time, which by mere application of heat recovers its original properties, and that without loss or gain in weight. It must,

therefore, be assumed that the altered properties exhibited under these circumstances result from a temporary rearrangement of its constituent particles. When, as in this case, elementary matter, stuff, or substance is capable of making its appearance in the form of two or more bodies having different properties, these are said to be *allotropic* modifications of the element, and the phenomenon is spoken of as allotropy. (See 'Isomerism and Allotropy,' Chapter IX.)

About seventy elements are known at the present time, but it is not improbable that a few new substances may be hereafter added to this number. It is not, however, very likely that any hitherto unknown elements will be found to occur in any considerable quantity among the constituents of the earth's crust, for every substance within reach of man has already been subjected to a very close scrutiny by chemists.

It will be seen by reference to the following table that the materials which compose the solid earth, so far as we know it—the ocean, the atmosphere, and the bodies of the living beings which inhabit it—are made up of a few of these elements, the rest occurring in much smaller quantity, in some cases are discoverable only by specially delicate methods.

Water consists of		Hydrogen. Oxygen.
Air consists chiefly of		Oxygen. Nitrogen.
Solid earth consists chiefly of	Silica =	Silicon. Oxygen.
	Limestone =	Calcium. Magnesium. Carbon. Oxygen.
	Various silicates forming crystalline rocks or beds of clay	Silicon. Oxygen. Aluminium. Iron. Calcium. Potassium.

Plants consist chiefly of	. . .	Carbon. Hydrogen. Oxygen.
Animals consist chiefly of	Soft Parts =	Carbon. Hydrogen. Oxygen. Nitrogen.
	Bone and Shell =	Calcium Phosphate. Calcium Carbonate.

The extraction of the metals from their ores, the manufacture of alkalies, soap, glass, dyes, and a variety of other useful applications of practical chemistry, were known to man in a more or less practical form from very early times. The alchemists extended the art of chemistry by the discovery of the processes for producing many acids and salts, and by the invention of much useful apparatus. The discovery of oxygen by Priestley, of chlorine by Scheele, the proof of the composition of water supplied by Cavendish, and the overthrow of the phlogistic theory by Lavoisier's explanation of combustion, were all great strides in advance which followed one another in rapid succession. But the foundation of chemistry as an exact science was only laid towards the end of the last century, when the balance began to be used systematically in all chemical investigations. Exact determinations of the relative weights of bodies engaged in various chemical reactions were necessary for the establishment of those laws upon which chemical ideas of the present day are founded. A long series of experiments was required before the facts were generally accepted by chemists. It was proved towards the end of the eighteenth century that acids and bases neutralise each other completely when limited and fixed proportions of each are mixed together, but these experimental results failed to attract the notice they deserved, and it was only about 1808 that the first and most important quantitative principle in

chemistry was finally established by the experiments of Proust. This is known as the 'Law of Definite Proportions,' and may be stated as follows :—

The proportions in which substances unite together are definite and constant. In other words, a given chemical compound always consists of the same elements united in the same proportions.

In order to form water, for example, union between hydrogen and oxygen occurs exactly in the proportion of two measures of the former to one measure of the latter. This corresponds with two parts by weight of hydrogen to sixteen parts by weight of oxygen, since oxygen is sixteen times heavier than hydrogen. The employment of any larger quantity of either element would only result in the excess being left uncombined.

When two bodies unite together to form a chemical compound they merge so completely one into the other as to be no longer recognisable by any physical character. The properties of chemical compounds are always quite distinct from those of their constituents, and in general have not even a remote resemblance to them. In the glistening red crystalline powder called by chemists mercuric oxide and vulgarly 'red precipitate,' no trace can be detected by the eye, or by any other sense, of the liquid, volatile, silvery metal mercury, and the colourless, gaseous oxygen into which it is resolved by the action of heat. In water, again, whether examined in the condition of solid ice, liquid water, or vaporous steam, we should look in vain for any resemblance to the gaseous elements, hydrogen and oxygen, of which it consists. Neither can we detect in the properties of water any that can be regarded as intermediate between those of the two constituents, or such as we should expect to find exhibited by a mixture in which each element retained its independence.

Every chemical compound is definite in its nature, and not only contains the elements of which it is composed in

proportions which are invariable, but it exhibits constant characters by which it may usually be identified. Water, for example, is a nearly colourless liquid at common temperatures, which contracts when cooled to about 4°, and if cooled further expands till it solidifies into ice. The melting point of ice is constant at 0°, and the boiling point of water under a pressure of one atmosphere is 100°. The melting points and boiling points of other substances are in like manner fixed temperatures, and their observation in the chemical laboratory is daily resorted to with the object of recognising and distinguishing substances already known or newly discovered.

The law of definite proportions itself furnishes a criterion by which the character of a body under examination may be judged as to its title to rank as a definite chemical species. For when it is found that the elements contained in a substance are united together in the ratio of their atomic weights (see Chapter III.), the probability that they are chemically combined is very great; whilst if they are not present in such proportion, the inference that the substance is a mixture is completely justified.

In order to decide whether a given substance is a true chemical compound or a mere mechanical mixture, various considerations are employed by chemists, the nature of which depends very much upon the circumstances of each particular case. If a solid body is the subject of investigation, it is examined under a microscope, in order to see if its appearance is uniform throughout; or, if crystallisable, it is recrystallised, and the crystals compared with those of the original substance. If soluble in any liquid, it may be treated with a quantity of the solvent insufficient to take up the whole. The part dissolved, after getting rid of the solvent by evaporation or otherwise, ought to agree in every respect with the undissolved portion, if the original body is one compound and not a mixture.

In the case of those liquids which are volatile, and which

bear the application of heat without decomposition, the boiling point should remain constantly at the same temperature during the distillation of the whole, and portions taken from the retort and from the distillate in the receiver ought, in the case of definite compounds, to correspond in density and all other physical and chemical characters.

When the body to be examined is a gas, the action of solvents is tried; and if, after such treatment, the relative proportions of the ingredients are undisturbed, the body may be regarded as probably consisting of one compound. This may be confirmed by observing whether these proportions agree with the combining weights of the elements present. The phenomena of gaseous diffusion are also frequently useful in helping to decide whether the elements in a given gas are chemically combined or mechanically mixed. Other means of a mechanical nature may be resorted to in special cases, and occasionally considerable ingenuity is called for in devising methods suited to the occasion.

One or two examples will render these matters more intelligible to the student. We will select cases in which the law of definite proportions would afford no assistance in the solution of the problem.

Fifty-six parts of iron would unite with thirty-two parts by weight of sulphur; but the two elements may be mixed together in the state of fine powder, without exerting upon each other any chemical action whatever, the compound, ferrous sulphide, which would be formed by their union in these proportions being produced only when they are strongly heated together. The *mixture* of these two bodies, though it might be indistinguishable from the compound by appealing to the proportions of the two ingredients, would yet be easily recognised by such properties as the following:—Under a microscope particles of iron and particles of sulphur would be visible; a magnet would withdraw the iron from the powder and leave the sulphur; carbon bisulphide would dissolve the sulphur, but would not affect the iron; a

separation could be effected by merely stirring up in water, when the iron, by reason of its greater density, would sink quickly to the bottom, leaving the sulphur suspended; diluted sulphuric acid poured upon the mixture would evolve hydrogen gas. The chemical *compound* has a uniform appearance under the microscope; if reduced to powder, it could not be divided into two different portions by the use of a magnet, by any solvent, or by elutriation with water; and, lastly, the action of diluted sulphuric acid would result in the evolution of hydrogen sulphide gas, easily distinguishable from hydrogen by its odour, by its solubility in water, and by many other properties.

The domain of organic chemistry supplies numerous problems of the kind we are considering.

In certain kinds of tartar there exist the potassium salts of two acids, which have the same composition, but somewhat different properties. These acids are called respectively tartaric and racemic acid. The former rotates the plane of polarisation of a ray of polarised light to the right, whilst the latter is optically inactive. Crystals of tartaric acid are permanent in the air, whilst those of racemic acid contain a molecule of water, which, escaping at ordinary temperatures, renders the crystals efflorescent. Racemic acid and calcium racemate are decidedly, though not very greatly, less soluble than the corresponding tartaric acid and calcium tartrate. Hence it will be perceived that whilst it is perfectly easy to distinguish the pure acids from each other, the mere estimation of the amount of carbon and hydrogen, or even an examination of a great many of the salts, would not suffice to decide between the one or the other of them and a mixture of the two.

A mixture of alcohol, water, and ether might be made in such proportions (46 : 18 : 74) that it would possess exactly the same composition as alcohol. But such a mixture would be at once distinguished from alcohol by its peculiar odour, and by separating into two layers on addi-

tion of water. When distilled, it would be found to boil at a much lower temperature than the boiling point of alcohol ; and after about three-fourths had passed over into the receiver, the liquid left behind in the retort would no longer smell of ether, and would be easily recognised as weak alcohol.

Again, the commercial liquid alkaloid toluidine is an oil which, when distilled, boils steadily at about 200°, and no difference of composition can be detected between the first portions of the distilled liquid and the last. And yet this substance is a mixture of two alkaloids of the same composition, one liquid, the other solid, the boiling points of which (200° and 198°) differ so slightly that they cannot be separated by any kind of fractional distillation. They can be completely separated from each other by taking advantage of the fact that the oxalate of solid toluidine is much less soluble in ether than the oxalate of the liquid base, or by the difference of properties of their acetyl derivatives or of their hydrochlorides. When the compounds obtained undergo no change in crystalline form or in solubility when recrystallised, they are believed to be pure and homogeneous. From the compounds thus separated the alkaloids themselves may be regenerated by appropriate treatment.

Examples of mixtures of gases, presenting the same composition as true chemical compounds, might be easily multiplied.

Thus, equal volumes of hydrogen and chlorine constitute a gaseous mixture which exhibits the colour and bleaching action of chlorine ; and after shaking up with solution of soda, just one-half its bulk of colourless inflammable hydrogen remains. Hydrogen chloride gas, which contains the same elements combined in the same proportions, is, on the contrary, a colourless gas which no longer possesses the bleaching power of chlorine, and is readily and completely soluble in water or in solution of soda.

Ethane and hydrogen gases in equal volumes furnish a mixture which would be indistinguishable from marsh gas by ordinary quantitative analysis. But recollecting that ethane is more than four times more soluble in water than hydrogen, whilst the rate of diffusion of hydrogen is nearly four times that of ethane gas, it would not be difficult to distinguish the mixture from the compound. Further assistance might be derived from a study of the action of chemical agents upon the two gases.

The case of atmospheric air is one of so great importance that its consideration demands some attention in this place.

Neglecting accidental constituents, as well as the water vapour, carbon dioxide and argon, which are always present, the analysis of air from various localities has led to the conclusion that it consists almost uniformly of 20·9 volumes of oxygen with 79·1 volumes of nitrogen. The question whether these two elements are united together chemically has been decided in the negative, in accordance with such considerations as the following :—

1. The most accurate analyses seem to indicate that the proportion of oxygen to nitrogen in the atmosphere is not absolutely uniform, as would be the case if it were a compound.

2. The quantities of oxygen and nitrogen present do not bear any simple relation to the combining weights of those elements.

3. When oxygen and nitrogen are mixed together they show no signs of chemical action by evolution of heat or contraction of volume ; and such a mixture, when due proportions are employed, resembles atmospheric air in every respect.

4. Water dissolves the constituents of the air in unequal proportions, so that, by reason of the greater solubility of oxygen, the air which may be expelled from common water by boiling contains a larger proportion of that element

than is present in atmospheric air. A chemical compound would dissolve, as a whole, without change of composition.

5. When the rays emitted from a given source of heat are transmitted through different gases, it is found that compounds absorb a much larger amount than elementary gases or mixtures of elementary gases. Thus the amount of radiant heat absorbed by nitrous oxide, a colourless and transparent gas, is more than 350 times as great as the amount absorbed by a column of equal length of oxygen, nitrogen, or atmospheric air. Between the absorbent powers of the last three gases no difference can be detected, and the natural inference, therefore, is that they are similarly constituted.

6. The elements may be separated to a certain extent by the mechanical process of diffusion through a porous plate, called, in this case, *atmolysis*.

It was also discovered by Graham (see Introduction, p. 21) that gases have the power of penetrating thin sheets of india-rubber, and that the rate at which oxygen passes through this material is more than two and a half times that of nitrogen. Upon this observation he based a very instructive experiment, which proves conclusively the fact that the oxygen of atmospheric air is not combined with the nitrogen. An air-tight india-rubber bag is exhausted as completely as possible by the Sprengel air-pump. When the exhaustion is nearly perfect, it is found that gas can still be slowly extracted from the bag by continuing the operation; and this gas is found by analysis to consist of a mixture of nitrogen and oxygen, containing upwards of 40 per cent. of the latter ingredient. The gases thus withdrawn from the bag result from the passage of the gases of the atmosphere through the india-rubber partition; the oxygen, however, more rapidly than the nitrogen. The explanation of this dialytic passage of gases through the apparently impermeable caoutchouc appears to be that the

gases are absorbed by the external surface of that material, that they penetrate in this condition to the other side of the sheet, where evaporation occurs in consequence of exposure to an atmosphere of very slight density.

CHAPTER II.

LAWS OF CHEMICAL COMBINATION.

THE first and fundamental principle observed in the formation of chemical compounds has already been stated in the preceding chapter as the Law of Definite Proportions. This was ultimately believed and acted upon by chemists generally in the early years of the nineteenth century, but its complete establishment was accomplished only as the result of a large number of experiments carried out with great care by a number of different persons. Previously to that time the composition of a few oxides and sulphides was known with tolerable accuracy, and the proportion of basic oxide to acidic oxide in some salts, such as carbonate of lime and carbonate of magnesia, had been determined. It was also known that acids and bases were capable of neutralising each other when mixed in certain definite proportions, any excess of one or other remaining uncombined. This was further supported by the observation, to which attention was drawn by Wenzel in 1777, that when two salts are mixed together they generally give rise to two other salts by exchange of components, and that this process follows definite proportions. When, for example, 142 parts by weight of sodium sulphate are dissolved in water and mixed with 331 parts by weight of lead nitrate two new salts are formed, namely, lead sulphate and sodium nitrate, in the proportions of 303 parts of the former to 170 of the latter, and that if a larger quantity of either of the original

pair be taken the excess remains unchanged. These observations, however, remained for many years almost unnoticed till the principle of definite proportions in combination was established by Proust.

Up to this time the results of analysis had been represented by numbers which expressed the proportion of each constituent in 100 parts of the compound. For example, in 100 parts of red oxide of copper there are—

	Parts
Copper	88·8
Oxygen	11·2
	100·0

In black oxide of copper :—

Copper	79·87
Oxygen	20·13
	100·00

In carbon monoxide :—

Carbon	42·85
Oxygen	57·14
	100·00

In carbon dioxide :—

Carbon	27·27
Oxygen	72·72
	100·00

Dalton discovered reciprocal and multiple proportions by stripping from them the disguise in which this mode of representing composition enveloped them. For by taking the proportion of some one of the elements in a series of similar compounds as unity, and ascertaining by calculation the proportions which the others bear to it, it is easy to show that these proportions are simple multiples one of another.

In the case of the two oxides of carbon, the composition

of which has just been stated; if we calculate the ratio of the oxygen to the carbon in both of them, we find the proportion in the second double that in the first. Thus, taking the carbon as unity—

	Carbon		Oxygen		Carbon		Oxygen
	42·85	:	57·14	::	1	:	1·33
and	27·27	:	72·72	::	1	:	2·66

Then plainly—

1·33	:	2·66	::	1	:	2

In other words, the proportion of oxygen by weight in carbon dioxide gas is double that contained in carbon monoxide. Obviously the same fact may be expressed in another way by taking the oxygen as unity instead of the carbon :—

Oxygen		Carbon		Oxygen		Carbon
57·14	:	42·85	::	1	:	·750
72·72	:	27·27	::	1	:	·375

Then—

·750	:	·375	::	2	:	1

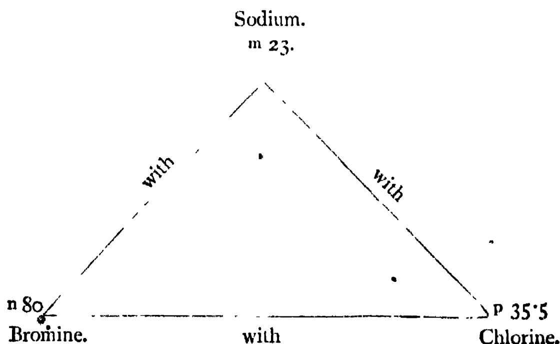
Or we may say that carbon dioxide contains half as much carbon as carbon monoxide. Similarly it will be found that the ratios of the oxygen in the several oxides of nitrogen, of sulphur, and of many of the metals are as 1, 2, 3, &c., to 1, 2, 3, &c., of the other constituent.

Hence it appears that *when two substances unite together in several proportions, then if one of them is taken as the unit the quantity of the other substance in the different compounds varies in a simple manner.* This is known as the Law of Multiple Proportions. A great number of equally simple cases might be cited, and, doubtless, it was the study of such cases which in the first instance led to the enunciation of the law. In perhaps a still greater number of instances, however, it is by no means easy to trace its application. Among the numerous compounds of carbon with hydrogen, for example, are found such relations as the following, which represent the composition of the series of paraffins :—

	Carbon		Hydrogen
Methane	3 parts	with	1 part
Ethane	4	,,	1 ,,
Propane	9	,,	2 parts
Butane	24	,,	5 ,,
Pentane	5	,,	1 part
Hexane	36	,,	7 parts
Heptane	21	,,	4 ,,
Octane	16	,,	3 ,,
Nonane	27	,,	5 ,,
Decane	60	,,	11 ,,
&c.	&c.		&c.

A third proposition known as the Law of Reciprocal Proportions, or the Law of Equivalents, may be stated as follows :—

The weights of two different elements, A and B, which combine with a third, C, represent the proportions in which they will themselves unite together if union between them is possible, or they bear some simple relation to those proportions. Thus, $35\frac{1}{2}$ parts of chlorine and 80 parts of bromine combine with 23 parts of sodium. Then, according to the law, when chlorine combines with bromine, $35\frac{1}{2}$ parts of the former are required for every 80 parts of the latter. This may be rendered graphically somewhat in this manner :—



In other words, the combining weight of a body may always be represented as a multiple of the same number whatever state of combination it enters into, or $m\,n$ is the combining weight, where m is a number peculiar to the body and n is some integer.

Looking round for an explanation of these facts, it occurred to Dalton about 1804 to resuscitate the ancient theory of the limited divisibility of matter. According to this view, matter is made up of definite small parts or particles which are called 'atoms' (see Introduction, p. 7), because it is assumed that they cannot be cut or divided, or at any rate are not divided in the course of ordinary chemical and physical changes. According to this view, chemical combination results from the approximation of atoms to one another, while chemical decomposition is due to their separation. It is obvious that the three laws of Definite, Multiple, and Reciprocal Proportions receive a full explanation from the Atomic Theory, for if we assume, for example, that the element oxygen is composed of atoms each having a definite mass, and that no fractional part of an atom can exist or take part in forming a compound, and if in like manner we assume that the element hydrogen is similarly constituted except that the atoms are of smaller mass, then when combination takes place between these two substances, 1, 2, 3, &c. atoms of one kind will unite with 1, 2, or 3, &c. atoms of the other kind. The absolute weights of atoms are not known, but their relative weights can be determined, and if the weight of an atom of hydrogen is represented by 1, the weight of an atom of oxygen is 16. Hence any compounds of oxygen with hydrogen must, if the hypothesis is correct, consist of 16 parts by weight of oxygen with 1 part by weight of hydrogen, or of $16 \times m$ parts of oxygen with $1 \times n$ parts of hydrogen, where m and n are whole numbers.

GAY-LUSSAC'S LAW OF VOLUMES.

When gases combine together they do so in equal volumes, or in volumes which have some simple relation one to another, as 1 to 2, 1 to 3, 2 to 3, and so on. For example, hydrogen chloride is formed by the union of

1 volume of hydrogen with
1 volume of chlorine ;

water is formed by the union of

2 volumes of hydrogen with
1 volume of oxygen ;

ammonia by the combination of

3 volumes of hydrogen with
1 volume of nitrogen ;

nitrogen trioxide by the combination of

2 volumes of nitrogen with
3 volumes of oxygen, &c.

It is important also to remember that whatever the volume of the vaporous elements before combination, the bulk of the resulting compound, measured in the gaseous state under the same conditions of temperature and pressure, is generally less than the total bulk of the constituent gases measured separately.

In a very few cases the volume occupied by the united substances is the same whether they are combined chemically or only mixed together.

Thus

1 volume of hydrogen with
1 volume of chlorine,

mixed together, would, of course, form only two volumes of the mixture, but when united they also produce

2 volumes of hydrogen chloride gas.

On the other hand,

1 volume of oxygen with
2 volumes of hydrogen

contract into

2 volumes of water gas.

This law of volumes was first announced by Gay-Lussac very soon after the laws of multiple and reciprocal proportions by weight had been established by Dalton. It should be clearly understood that all these statements were originally the outcome of experiment, and were unconnected with any previous hypothesis as to the constitution of matter. We now see that if Avogadro's hypothesis as to the constitution of gases (Introduction, p. 16) is accepted, the law of volumes arising out of Gay-Lussac's experiments may be explained by the application of the Atomic Theory nearly in the same way as the multiple and reciprocal relations discovered by Dalton. Suppose, for example, 1 volume of hydrogen to contain n atoms, then according to Avogadro 1 volume of chlorine will also contains n atoms, and 2 volumes of hydrogen chloride contain $2n$ atoms of the compound. Similarly, if 1 volume of oxygen contains n atoms of that element, 2 volumes of hydrogen contain $2n$ atoms of hydrogen, and 2 volumes of water in the state of gas contain $2n$ atoms of water. Since the days of Dalton and Avogadro the convenient custom has arisen of distinguishing the primary particles or atoms which are separable from one another by chemical processes from the molecules which usually consist of united atoms, but this distinction does not affect the application of Dalton's Atomic Theory. A molecule of water, though universally believed to consist of two atoms of hydrogen combined with one atom of oxygen, is none the less in the strict sense of the term an *atom* of water, for if divided into smaller parts it ceases to be water, and becomes oxygen and hydrogen.

CHAPTER III.

SYMBOLS AND FORMULÆ.

The introduction of the Atomic Theory led immediately to the employment of a system of symbols having a quantitative significance, by which the atoms of elements and their union in various proportions to form compounds could be clearly expressed. The symbols used by Dalton consisted of circles bearing arbitrary marks for the sake of distinction: thus the symbol of an atom of hydrogen was ⊙, while an atom of oxygen was represented by ○, and an atom of nitrogen by ⦶. The symbols of elements placed near together indicated chemical combination: an atom of water, for example, was supposed to consist of an atom of hydrogen combined with an atom of oxygen, thus ⊙○.

Dalton's symbols, however, soon gave place to a more convenient system introduced by Berzelius, which, with slight modifications in a few individual cases, has been used down to the present day.

To each of the elements is assigned a symbol formed generally of the initial letter of the Latin name of the element. For example, sulphur is represented by the symbol S; selenion, Se; silicon, Si; strontium, Sr; but silver (*argentum*) is Ag, and sodium (*natrium*) has the symbol Na.

But chemical symbols are not merely abbreviations contrived, like shorthand characters, for the purpose of saving trouble in writing the names. Each symbol represents *one atom* of the element for which it stands, and hence expresses a definite weight and volume of the element, which are identical with the proportions by weight and volume in which it enters into chemical combination.

The weight of an atom of hydrogen is less than the weight of an atom of any other element. It is, therefore, convenient to consider the value of the symbol of hydrogen as unity and the values of all other symbols greater than unity. But since nothing is known as to the absolute weight of an atom of hydrogen or of any other element, it should be borne in mind that the atomic weights are in reality ratios, or fractions whose denominator is 1, although they are always written in the form of whole numbers.

In the following list are given the names of all the known elements, together with their symbols and atomic weights, but it will be observed that, in addition to the first column, which contains the atomic weight calculated from the most trustworthy data and compared with hydrogen taken as the unit, two other columns have been added in which the numbers have been increased in the proportion of 15·88 to 16. The object of this is to provide for ordinary purposes a set of numbers which more nearly approach to integers, and are therefore more easily remembered and more convenient for purposes of calculation. Strictly speaking, this change, which gives to oxygen the atomic weight 16, a whole number, makes the atomic weight of hydrogen greater than 1, but as the difference is very small it is customary, when great accuracy is not an object, to take no account of this difference. The student is recommended at once to commit to memory the numbers given in the third column opposite to those names which are printed in capital letters, leaving the rest to be learnt gradually as occasion may require.

In a later chapter an account will be given of the methods by which the numerical values of the atomic weights are determined.

TABLE OF ATOMIC WEIGHTS.

Name of Element.	Symbol.	Calculated from the most accurate Experiments.		Approximate Values for Common Use.
		(H = 1)	(O = 16)	(O = 16)
ALUMINIUM	Al	26·9	27·1	27
Antimony	Sb (Stibium)	119·1	120	120
Argon	A	39·6	40	40
Arsenic	As	74·4	75	75
Barium	Ba	136·4	137·4	137
Beryllium	Be	9·03	9·1	9·1
Bismuth	Bi	206·9	208·5	208
Boron	B	10·9	11	11
BROMINE	Br	79·36	79·96	80
Cadmium	Cd	111·6	112·4	112
Cæsium	Cs	132	133	133
CALCIUM	Ca	39·7	40	40
CARBON	C	11·91	12	12
Cerium	Ce	139	140	140
CHLORINE	Cl	35·18	35·45	35·5
Chromium	Cr	51·7	52·1	52
Cobalt	Co	58·56	59	59
COPPER	Cu (Cuprum)	63·1	63·6	63·5
Erbium	E	164·7	166	166 ?
FLUORINE	F	18·9	19	19
Gadolinium	Gd	155	156	156 ?
Gallium	Ga	69·5	70	70
Germanium	Ge	71·5	72	72
GOLD	Au (Aurum)	195·7	197·2	197
Helium	He	4	4	4
HYDROGEN	H	1	1·008	1
Indium	In	113·1	114	114
IODINE	I	125·9	126·85	127
Iridium	Ir	191·5	193	193
IRON	Fe (Ferrum)	55·6	56	56
Krypton	Kr	81·2	81·5	82 ?
Lanthanum	La	137	138	138
LEAD	Pb (Plumbum)	205·35	206·9	207
Lithium	Li	6·98	7·03	7
MAGNESIUM	Mg	24·18	24·36	24·3
Manganese	Mn	54·6	55	55
MERCURY	Hg (Hydrargyrum)	198·8	200·3	200
Molybdenum	Mo	95·3	96	96
Neodymium	Nd	142·5	143·6	144 ?

Name of Element.	Symbol.	Calculated from the most accurate Experiments.		Approximate Values for Common Use.
		(H = 1)	(O = 16)	(O = 16)
Neon . . .	Ne . .	19·9	20	20 ?
Nickel . .	Ni . .	58·3	58·7	58·7
Niobium . .	Nb . .	93·3	94	94 ?
NITROGEN .	N . . .	13·93	14·04	14
Osmium . .	Os . .	189·6	191	191
OXYGEN . .	O . . .	15·88	16	16
Palladium . .	Pd . .	105·2	106	106
PHOSPHORUS	P . . .	30·77	31	31
Platinum . .	Pt . .	193·3	194·8	195
POTASSIUM .	K (Kalium) .	38·86	39·15	39
Praseodymium .	Pr . .	139·4	140·5	140 ?
Rhodium . .	Ro . .	102·2	103	103
Rubidium . .	Rb . .	84·76	85·4	85
Ruthenium. .	Ru . .	100·9	101·7	102
Samarium . .	Sm . .	148·9	150	150 ?
Scandium . .	Sc . .	43·8	44·1	44
Selenion . .	Se . .	78·5	79·1	79
SILICON . .	Si . .	28·2	28·4	28
SILVER . .	Ag (Argentum)	107·12	107·93	108
SODIUM . .	Na (Natrium)	22·88	23·05	23
Strontium . .	Sr . .	86·94	87·6	88
SULPHUR .	S . . .	31·83	32·06	32
Tantalum . .	Ta . .	181·6	183	183 ?
Tellurium . .	Te . .	126	127	127 ?
Terbium . .	Tb . .	158·8	160	160 ?
Thallium . .	Tl . .	202·6	204·1	204
Thorium . .	Th . .	230·8	232·5	233
Thulium . .	Tm . .	170	171	171 ?
Tin . . .	Sn (Stannum)	117·6	118·5	119
Titanium . .	Ti . .	47·7	48·1	48
Tungsten . .	W (Wolfram) .	182·6	184	184
Uranium . .	U . . .	237·7	239·5	240
Vanadium . .	V . . .	50·8	51·2	51
Xenon . . .	Xe . .	127	128	128 ?
Ytterbium . .	Yt . .	172	173	173 ?
Yttrium . .	Y . . .	88·3	89	89 ?
ZINC . . .	Zn . .	64·9	65·4	65
Zirconium . .	Zr . .	90	90·7	91

In order to indicate combination between two elements their symbols are placed side by side, thus, HCl. When a molecule of a compound contains more than one atom of each or either of its constituents, the number of atoms is indicated by a small figure placed below the line.

Thus the formula for water, OH_2, represents one atom of oxygen united with two atoms of hydrogen, and H_3PO_4 means that three atoms of hydrogen, one atom of phosphorus, and four atoms of oxygen are bound together in phosphoric acid.

The formula, taken as a whole, is generally assumed to represent *a molecule* of the compound, though it will hereafter (Chapter VI.) be explained that much uncertainty exists in many cases. The relative weight of the molecule is easily found by adding together the weights represented by the several symbols of which it is made up. This weight is called the molecular weight. In order to express two or more molecules a figure is placed at the beginning of the formula, and must be understood to multiply every symbol that follows it. For example, $2OH_2$ represents two molecules of water, each consisting of two atoms of hydrogen with one atom of oxygen; in all, four atoms of hydrogen and two atoms of oxygen. Occasionally brackets have to be introduced when some group of symbols occurs more than once. Aluminium sulphate, for example, has the formula $Al_2(SO_4)_3$, which is thus written for the sake of assimilating the appearance of the formula to that of other sulphates, such as H_2SO_4, $BaSO_4$, $FeSO_4$, &c. Resemblance between them would be less apparent if it were expressed as $Al_2S_3O_{12}$.

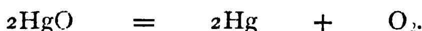
Care and a little practice are all that is necessary to avoid confusion in the use of formulæ, and the beginner is therefore recommended to work out conscientiously all the examples given at the end of the section.

Equations.—Chemical changes involve neither the destruction nor the creation of matter, but simply a redis-

tribution of the materials of which the acting masses are composed. In order, therefore, to represent by symbols the results of any given change, it is only necessary to write down the formulæ of the substances concerned, and then to transpose their symbols in such a manner as to build up the formulæ of the compounds which are produced. We thus arrive at equations in which the signs +, – and = are employed so far as the weights of matter are concerned, in the same sense as in algebra.

The following examples will serve to show the manner in which chemical equations are to be read, as well as the mode of investigating the relative weight of the bodies which are formed or decomposed. The student should practise reading equations aloud, or writing them out at full length, according to these instructions:—

Equation given,



$$2HgO = 2Hg + O_2.$$

This means that two molecules, or 432 parts, by weight, of mercuric oxide yield two molecules, or 400 parts, by weight, of metallic mercury, and one molecule, or 32 parts, by weight, of oxygen.

Young students, however, would do well to ensure precision by filling up such a scheme as the following:—

	$2HgO$	=	$2Hg$	+ O_2
No. of molecules	2	give	2	and 1
Name . .	Mercuric oxide		Mercury	Oxygen
Wt. of 1 mol. .	200 + 16 = 216		200	32
Whole weight .	used 432		obtained 400	32

When gases or vaporisable bodies occur in such an equation we can express the volume of each by recollecting that, according to the law of Avogadro, the space occupied by a gaseous molecule under normal conditions is always the same. We may also connect together the weight and volume of a gas by applying a rule which will be more fully ex-

plained in the next section, namely, that the relative density of a body in the gaseous state[1] is the half of its molecular weight. The weight of a molecule of carbon dioxide, for example, is 44; its relative density is, therefore, 22, and the weight of a litre of the gas is 22 times as great as the weight of a litre of hydrogen measured at the same temperature and pressure. Now, the weight of a litre of hydrogen at 0° C., and under a pressure equal to 760 mm. of the barometric column, is very nearly ·09 gram or 1 crith. Hence we may say that a litre of carbon dioxide weighs 22 criths, or, if the weight is to be expressed in grams, it will be 22 × ·09 grams.

Example:

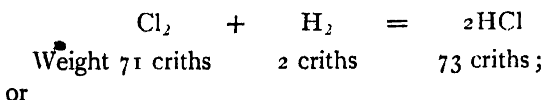


$$Cl_2 + H_2 = 2HCl.$$

A molecule of chlorine and a molecule of hydrogen produce two molecules of hydrogen chloride.

	Cl_2	+	H_2	=	$2HCl$
No. of molecules	1		1		2
Name . .	Chlorine		Hydrogen		Hydrogen chloride
Wt. of 1 molecule	71		2		36·5
Whole weight .	used 71		2		obtained 73
Volume . .	,, 1		1		obtained 2
	or 2		or 2		or 4

If, now, we choose to attach a concrete value to the symbols, we express it thus:



$$Cl_2 \quad + \quad H_2 \quad = \quad 2HCl$$

Weight 71 criths   2 criths   73 criths;

or

71 × ·09 grams + 2 × ·09 gram = 73 × ·09 grams

Vol. 2 litres + 2 litres = 4 litres.

The student having throughly mastered the foregoing examples, and worked some of the exercises given at the

[1] The density of hydrogen being taken as 1.

end of the section, is now in a position to solve such problems as the following, which may be taken as representative :—

1. How many pounds of zinc are required to make 500 pounds of the crystallised sulphate?

Formula of one molecule of crystallised zinc sulphate, $ZnSO_4 . 7H_2O$.

Molecular weight 287.

The symbol of zinc, Zn = 65, occurs only once in the formula of the sulphate. Hence,

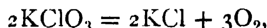
In 287 lbs. of zinc sulphate there are 65 lbs. of zinc.

1 lb. „ „ „ $\frac{65}{287}$ lb. of zinc.

∴ 500 lbs. „ „ would require $\frac{65}{287} \times 500$ lbs.

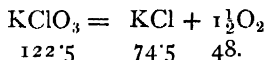
Ans. $\frac{65 \times 500}{287} = 113$ lbs. $3\frac{7}{8}$ oz. of zinc.

2. How many litres of oxygen (at standard temperature and pressure) are obtained by heating 10 grams of potassium chlorate?



$$2KClO_3 = 2KCl + 3O_2,$$

or more simply



$$\underset{122 \cdot 5}{KClO_3} = \underset{74 \cdot 5}{KCl} + \underset{48.}{1\tfrac{1}{2}O_2}$$

Taking the potassium chlorate in criths, we should obtain 3 litres of oxygen gas.

Then—

122·5 criths,

or 122·5 × ·09 grams give 3 litres of oxygen.

1 gram would give $\frac{3}{122 \cdot 5 \times \cdot 09}$ litres.

∴ 10 grams „ „ $\frac{30}{122 \cdot 5 \times \cdot 09}$ litres.

Ans. $\frac{30}{122 \cdot 5 \times \cdot 09} = 2 \cdot 721$ litres, or 2721 c.c.

Taking ·09 gram as the weight of 1 litre of hydrogen, 1 gram is the weight of 11·1 litres. This number is often useful. Thus, in the example worked out on the preceding page, the calculation would be a trifle shorter, thus :

$KClO_3$	give O_3
122·5 grams	16 × 3 grams
	or 11·1 × 3 litres.

Then 10 grams of chlorate would give

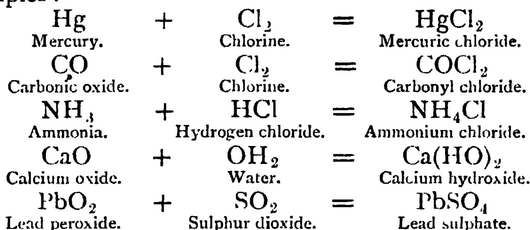
$$\frac{33 \cdot 33 \times 10}{122 \cdot 5} = 2 \cdot 72 \text{ litres.}$$

CLASSIFICATION OF REACTIONS.

Chemical action may take place in a great many different ways, but every known chemical change may be referred to one or other of the following five typical modes of action :—

I. *Combination of entire molecules.*

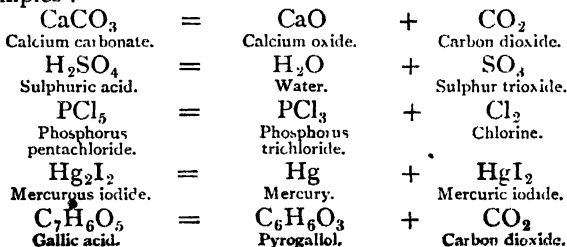
Examples :



Hg Mercury.	+	Cl_2 Chlorine.	=	$HgCl_2$ Mercuric chloride.
CO Carbonic oxide.	+	Cl_2 Chlorine.	=	$COCl_2$ Carbonyl chloride.
NH_3 Ammonia.	+	HCl Hydrogen chloride.	=	NH_4Cl Ammonium chloride.
CaO Calcium oxide.	+	OH_2 Water.	=	$Ca(HO)_2$ Calcium hydroxide.
PbO_2 Lead peroxide.	+	SO_2 Sulphur dioxide.	=	$PbSO_4$ Lead sulphate.

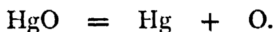
II. *Splitting up of a compound molecule into its elements, or into simpler molecules.*

Examples :



$CaCO_3$ Calcium carbonate.	=	CaO Calcium oxide.	+	CO_2 Carbon dioxide.
H_2SO_4 Sulphuric acid.	=	H_2O Water.	+	SO_3 Sulphur trioxide.
PCl_5 Phosphorus pentachloride.	=	PCl_3 Phosphorus trichloride.	+	Cl_2 Chlorine.
Hg_2I_2 Mercurous iodide.	=	Hg Mercury.	+	HgI_2 Mercuric iodide.
$C_7H_6O_5$ Gallic acid.	=	$C_6H_6O_3$ Pyrogallol.	+	CO_2 Carbon dioxide.

Many familiar decompositions, which at first sight appear to belong to this class, are in reality double decompositions, as an examination of one or two cases will show. The decomposition of mercuric oxide by heat, for example, seems to consist in a simple resolution of the compound into its elements,



$$HgO = Hg + O.$$

But when we write the equation molecularly,



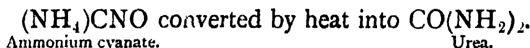
$$HgO + HgO = Hg + Hg + O_2,$$

we may see that the decomposition of one molecule of the oxide necessitates the splitting up of another. In order to form one molecule of oxygen—and we believe one molecule to be the smallest quantity of the element capable of independent existence—we must take two atoms of it from two separate molecules of the oxide.

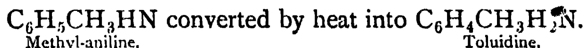
The same remarks apply to other cases, such as the decomposition of potassium chlorate by heat.

III. *Rearrangement of the atoms constituting a molecule so as to give rise to a new compound.*

Two examples of this mode of transformation may be given here.



$(NH_4)CNO$ (Ammonium cyanate) converted by heat into $CO(NH_2)_2$ (Urea).

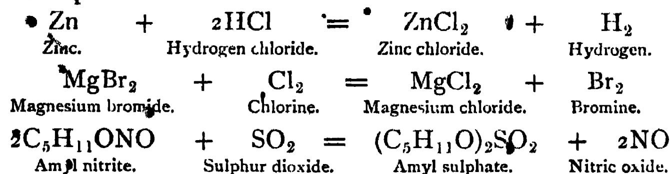


$C_6H_5CH_3HN$ (Methyl-aniline) converted by heat into $C_6H_4CH_3H_2N$ (Toluidine).

The further explanation of this kind of change is postponed to the chapter on 'Isomerism.'

IV. *Single Displacement.*—In this kind of change an atom, or group of atoms, contained in a molecule is displaced by another atom or group.

Examples :

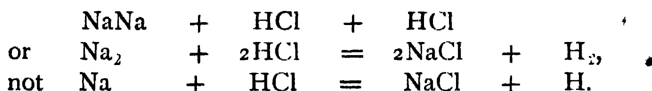


$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Hydrogen chloride.}}{2HCl} = \underset{\text{Zinc chloride.}}{ZnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

$$\underset{\text{Magnesium bromide.}}{MgBr_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Magnesium chloride.}}{MgCl_2} + \underset{\text{Bromine.}}{Br_2}$$

$$\underset{\text{Amyl nitrite.}}{2C_5H_{11}ONO} + \underset{\text{Sulphur dioxide.}}{SO_2} = \underset{\text{Amyl sulphate.}}{(C_5H_{11}O)_2SO_2} + \underset{\text{Nitric oxide.}}{2NO}$$

Many cases of precisely the same character are not easy to find. The fact is, the great majority of reactions belong to the next class of *double* decompositions. Even some which seem to be single decompositions must in strictness be so considered ; thus, the decomposition of hydrogen chloride by sodium must be represented in this manner ;



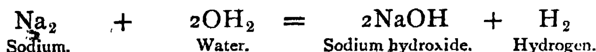
$$NaNa + HCl + HCl$$

or $$Na_2 + 2HCl = 2NaCl + H_2,$$

not $$Na + HCl = NaCl + H.$$

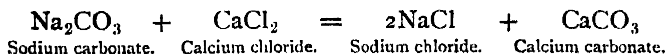
V. *Double Decomposition or Metathesis.*—This is by far the most general mode of action. Two or more molecules coming together exchange some of their constituents so as to give rise to the same number or to a greater number of molecules. We may, for the sake of completeness, classify double decompositions under three divisions :—

1. Those in which one of the reacting bodies is an element ; e.g.



$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Sodium hydroxide.}}{2NaOH} + \underset{\text{Hydrogen.}}{H_2}$$

2. Those in which both are compounds ; e.g.

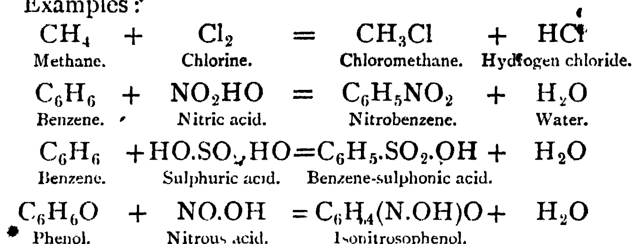


$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Calcium chloride.}}{CaCl_2} = \underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

3. Those which result in the formation of 'substitution' compounds. This kind of reaction is not essentially different in its nature from cases 1 and 2, but substitution

products among carbon compounds constitute a class of bodies so remarkable in their characters as to deserve special notice. Some examples of their formation are given in this place, more particular mention being reserved for a later chapter.

Examples:



CH_4	+	Cl_2	=	CH_3Cl	+	HCl
Methane.		Chlorine.		Chloromethane.		Hydrogen chloride.
C_6H_6	+	NO_2HO	=	$C_6H_5NO_2$	+	H_2O
Benzene.		Nitric acid.		Nitrobenzene.		Water.
C_6H_6	+	$HO.SO_2.HO$	=	$C_6H_5.SO_2.OH$	+	H_2O
Benzene.		Sulphuric acid.		Benzene-sulphonic acid.		
C_6H_6O	+	$NO.OH$	=	$C_6H_4(N.OH)O$	+	H_2O
Phenol.		Nitrous acid.		Isonitrosophenol.		

The study of the conditions under which chemical changes occur, and of such as retard or prevent change, is much more difficult, and will be referred to later in the book.

CHAPTER IV.

NOMENCLATURE.

A NAME may be used either for the purpose of indicating some particular person or object, or it may serve to point out relationships and to define the position which a thing holds in some system of classification.

In the early days of chemistry the number of different bodies known was comparatively small, and mere indicative names fulfilled all the requirements of the time. But when chemical research began to be regularly followed, and crowds of new compounds were constantly presenting themselves, it became necessary to devise names which would serve, not merely to distinguish one compound from

another, but to indicate, at least in some degree, the relationship subsisting between allied bodies. The first attempts of this kind were naturally imperfect, the devices employed being wholly inadequate to the requirements of the case. For example, it soon became evident that the mere employment of adjectives, as in the names *blue*, *green*, and *white* vitriol and the like, could have only a very limited application.

It was only after oxygen had been discovered, and its compounds were called *oxides* by Lavoisier, that chemical names began to assume some appearance of precision. The nomenclature adopted by the leading chemists of that period has met with very general acceptance ; and, although modified in detail, the system of the present day is based essentially upon the same principle. The names now employed by chemists for scientific purposes sometimes assume rather formidable dimensions, but, unlike the fanciful names in use in connection with some branches of natural history, every syllable has a significance of its own. And in spite of their length and frequent uncouthness, it may fairly be claimed for these names that they are in few cases inconvenient practically, while they do very fairly realise the idea originated by Lavoisier, namely, that of representing as by a formula the composition of the bodies for which they stand.

Nevertheless, many of the old names dating their origin from the times of the alchemists have become, by long familiarity, so incorporated into the language of medicine, of commerce, and the arts, that it is neither possible nor advisable for the chemist to reject their use. In the majority of cases, indeed, they are very serviceable, and no chemical student should disdain to make himself acquainted with such terms as *caustic potash*, *alum*, *borax*, *oil of vitriol*, *wood-spirit* and *marsh-gas*, and to use them when they express all that is required, alternatively with the more formal and systematic names, the employment of which, for certain

purposes, has been rendered necessary by the advance of knowledge.

Names of Elements.—Seven metals have been known from very early times, namely, gold, silver, quicksilver or mercury, lead, copper, iron, and tin, and as the names of these elements differ in modern languages, the Latin words are generally employed in the derivation of the symbols used in chemistry. These have already been given in the table of atomic weights (pp. 51, 52). Those elements which have been discovered by more modern chemical research have received names which in some cases recall their origin, *e.g.* silicon (*silex*, flint); whilst others were suggested by some prominent characteristic, *e.g.* chlorine (χλωρός, green), or by their chemical relations, real or supposed, *e.g.* oxygen (ὀξύς, acid; γεννάω, I generate).

Metals which have been discovered in modern times have all been designated by Latinised names, with the termination 'ium'[1]—potassium, sodium, lithium, thallium, &c.—while the names of the non-metallic elements are characterised by no syllable which is common to them all.

Names of Binary Compounds.—When two elements are combined together, the last syllable or two of the name of one of them is changed into the suffix *ide*. Thus, we have CaO, calcium oxide; HCl, hydrogen chloride; PbS, lead sulphide. In nearly all cases it is the name of the more negative or chlorous element which is thus modified, the name of the metal or corresponding element remaining unaltered.

Prefixes from the Greek—mono-, di-, tri-, &c.—serve to

[1] Unfortunately this termination has been erroneously applied to the name of the non-metal selenium, from a belief entertained at the time of its discovery that it was a metal. I have ventured in these pages to change the final syllable into *on*, selenion. The alteration of the name silicium into silicon will, I hope, be considered sufficient precedent.

indicate the number of atoms of the chlorous element present in a molecule of the compound. Thus—

N_2O is nitrogen monoxide.
N_2O_2 „ nitrogen dioxide.
N_2O_3 „ nitrogen trioxide.
N_2O_4 „ nitrogen tetroxide.
N_2O_5 „ nitrogen pentoxide.

Not unfrequently, however, when the actual number of atoms is doubtful, or when it is desired simply to indicate a relation between two compounds, that which contains the larger proportion of the chlorine or oxygen or similar substance is distinguished by the suffix *ic*, whilst the other ends in *ous*. Thus, in the foregoing series, we may distinguish—

N_2O as nitr*ous* oxide.
N_2O_2, or more correctly NO, as nitr*ic* oxide.

Similarly-

N_2O_3 is nitr*ous* anhydride.
N_2O_5 is nitr*ic* anhydride.

A few other marks serve in special cases; thus, Fe_2O_3, Cr_2O_3, Mn_2O_3, Al_2O_3, are often called *sesqui*oxides.[1] When there is a series of oxides, chlorides, or sulphides of the same elements, the syllables *proto*[2] and *per*[3] are sometimes prefixed to the name to indicate respectively the poorest and the richest in oxygen, chlorine, or sulphur, as the case may be. Thus, the two oxides of iron, which are usually represented by the formulæ FeO and Fe_2O_3, may be distinguished by one or other of the following pairs of names, according as it is desired simply to indicate that the ratio of oxygen to iron is greater in the one compound than in the other; or to imply, what is a matter of far less certainty,

[1] Latin, *sesqui*, one and a half. [2] Greek, *πρῶτος*, the first.
[3] Greek, *ὑπὲρ*, above, over, exceeding.

that so many atoms of the two elements form one molecule of the compound.

FeO, Ferrous oxide : Iron protoxide ; Iron monoxide ;
or or
Protoxide of iron. Monoxide of iron.

Fe_2O_3, Ferric oxide : Iron peroxide ; Iron sesquioxide ;
or or
Peroxide of iron. Sesquioxide of iron.

Names of Acids and Salts.—The same principles guide the construction of the names of these compounds, and a single example will go far towards explaining their application. It happens, in the case of chlorine, that an unbroken succession of compounds is formed by the union of this element with hydrogen and oxygen. These are their names and formulæ:

$HClO$ . . .	Hypochlorous acid.
$HClO_2$ . . .	Chlorous acid.
$HClO_3$ . . .	Chloric acid.
$HClO_4$ . . .	Perchloric acid.

Here, again, the terminations *ous* and *ic* serve to indicate different grades of oxidation, whilst the prefixes *hypo* and *per* respectively announce a smaller and a larger amount of oxygen than is contained in the chlorous and chloric acids. If we consent to regard acids as salts of hydrogen, we may write names for this series of compounds which are constructed in all respects in the same manner as those which are applied to salts in general.

Instead of	We may write
Hypochlorous acid . .	Hydrogen hypochlorite.
Chlorous acid . . .	Hydrogen chlorite.
Chloric acid . . .	Hydrogen chlorate.
Perchloric acid . . .	Hydrogen perchlorate.

And here another rule must be attended to, namely, that when the name of a salt ends in *ite*, the name of the acid or hydrogen salt with which it corresponds terminates in *ous*, whilst salts in *ate* are derived from acids whose names end in *ic*.

One more example will serve to emphasise this rule :

H_2SO_3	Hydrogen sulphite, or sulphurous acid.
$NaHSO_3$	Sodium-hydrogen sulphite, or acid sulphite of sodium.
Na_2SO_3	Disodium sulphite (normal), or sodium sulphite.
H_2SO_4	Hydrogen sulphate, or sulphuric acid.
$NaHSO_4$	Sodium hydrogen sulphate, or acid sulphate of sodium.
Na_2SO_4	Disodium sulphate (normal), or sodium sulphate.

In the name hydrochlor*ic* acid it is evident that the termination has nothing to do with the presence or absence of oxygen, and this use of the termination forms an exception to the general rule. It is convenient in this case to call the compound hydrogen chloride, and to reserve the old-established name, hydrochloric acid, for the familiar solution in water.

NAMES OF CARBON COMPOUNDS.

The nomenclature of carbon compounds has always been a subject involving much difficulty in consequence of the very large and rapidly increasing number of such compounds known to the chemist. With regard to those which have been known for a long time, the names are in the majority of cases fanciful, and generally have some reference either to the original source of the compound, or to some more or less prominent characteristic. Thus, formic acid is so called because it was originally obtained by distilling

ants (*formica*, an ant) with water, acetic acid because it was produced from vinegar (*acetum*), succinic acid because it is the acid obtained by distillation of amber (*succinum*), and lactic acid because it was extracted from sour milk (*lac*). Obviously no system of names could be contrived so long as the things to be named were not arranged in series and were apparently unconnected with one another.

The first step may be considered to have been taken when Liebig and Wöhler in 1832 showed that benzoic acid, essence of bitter almonds, and a number of other compounds contained a group of elements to which they gave the name 'benzoyl,' that is, benzoic stuff or matter (ὕλη). But the first practical proposal for reducing to some degree of order the very numerous compounds of carbon and hydrogen was made by Hofmann many years later. The number of atoms of carbon in the series of paraffins is indicated after the first three terms by incorporating the Greek numerals into the name, while the vowel *a* in the last syllable recalls the fact that these are the compounds saturated with hydrogen from which the succeeding members of each connected series may be derived by removing pairs of atoms of hydrogen. The latter are distinguished by the other vowels in the usual order. In the following table the names 'methane, ethane, propane,' are based upon the names of the radicles 'methyl, ethyl, propyl,' which have been long in use and are too familiar to be discarded :—

CH_4 Methane.	CH_2 Methene.		
C_2H_6 Ethane.	C_2H_4 Ethene.	C_2H_2 Ethine.	
C_3H_8 Propane.	C_3H_6 Propene.	C_3H_4 Propine.	C_3H_2 Propone.

The succeeding terms run : tetrane, pentane, hexane, heptane, octane, enneane, decane, &c.

Further successive attempts have been made to systema-

tise by restricting the use of certain terminations to the names of well-defined classes of compounds, and it is now generally agreed that the name should express the chemical functions of the compound, and thus serve as a kind of condensed formula.

In accordance with this principle the terminal syllable *ol* is reserved for alcohols and compounds resembling them; for example, carbinol, phenol, terpineol, thymol. Basic nitrogenous compounds are represented by names ending in *ine*, thus: ethylamine, quinine, strychnine. It is also the custom to use prefixes of Greek origin, such as *ortho*, *meta*, *para*, and to introduce numerals and Greek letters such as α, β, γ, δ, and Δ into the midst of the syllables composing the name with the object of indicating the supposed order of the components, but these are of course expressive of theoretical ideas of constitution which cannot be explained without reference to a large number of examples, and would indeed be appropriate only to a work exclusively devoted to the chemistry of carbon compounds.

CHAPTER V.

ATOMIC WEIGHTS.

THE first step towards the determination of the ratios, commonly called atomic weights, is to ascertain the proportions in which the several elements unite with some one of their number, the combining proportion of which is either taken as the unit, or whose ratio of combination has already been determined. With this object the form of experiment must be suitably chosen, and every precaution taken against error, which, however, can never be wholly avoided, even by the most skilful and experienced operators.

Oxygen was formerly employed as the standard of comparison, and its atomic weight taken as 100. But, since hydrogen is known to enter into combination in smaller proportion than any other element, it is more convenient to adopt it as the standard, and take its atomic weight as unity. The most important relation to establish at the outset is the proportion in which oxygen and hydrogen unite together to form their most stable and characteristic compound, water. This has been attempted by a number of experimenters, but notwithstanding all the care and labour which have been spent upon the investigation, it can hardly be said that the values obtained represent so accurately the combining ratios of these two elements that further experiment is unnecessary.

Two chief methods have been adopted. Dumas, in 1842, published the result of his experiments, the first which were conducted with any near approach to accuracy. His plan consisted in passing pure hydrogen through a weighed bulb containing pure oxide of copper heated to redness, collecting the water thus formed and weighing it. Assuming the value 1 for the atomic weight of hydrogen, Dumas obtained for oxygen the number 15·9607. Erdmann and Marchand by the same process obtained the value 15·9733. The second important method consists in determining directly the relative densities of the two gases by weighing them in large globes. By this mode of operating Regnault found oxygen to be 15·9628 times heavier than hydrogen. There can be no doubt, however, that the density of oxygen is somewhat less than this. Lord Rayleigh's experiments in 1893 made it 15·882, while those of Professor E. W. Morley gave the number 15·895, and reviewing the work of other experimenters the results stand as follows. The mean value of the symbol O derived from the synthesis of water is 15·8796, while from a comparison of the densities of oxygen and hydrogen with that of air its value is 15·8769. The general mean is 15·8794, from which the number 15·88

differs inappreciably, and it may be used for all scientific purposes.

The most trustworthy estimations of the combining weight of carbon were made by the simple method of burning a weighed quantity of pure carbon, in the form of graphite or diamond, in oxygen, and collecting the carbon dioxide formed by means of caustic potash contained in suitable absorption apparatus, carefully weighed. In carbon dioxide 16 parts of oxygen combine with 6 parts of carbon almost exactly; but assuming the value 15·88, already given for oxygen, the combining weight of carbon becomes 11·913.

For the estimation of the combining proportions of other elements different methods have to be adopted. It will be sufficient if two or three of these are indicated. Chlorine, potassium, and silver may be taken as being both important and representative.

By decomposing potassium chlorate by heat or by hydrochloric acid, and weighing the resulting potassium chloride, experiments conducted at different times by Berzelius, Penny, Marignac, and Stas led to results the general mean of which gave 60·846 parts of potassium chloride from 100 parts of potassium chlorate. This may be expressed as follows:—

Potassium chloride : oxygen :: 60·846 : 39·154,

or $KCl : O_3 :: 74{\cdot}4217 : 47{\cdot}8899$.

This number, 74·4217, is the combining weight of potassium chloride, and is made up of the combining weights of potassium and chlorine. These must be separately estimated as follows. Starting with pure silver, it may be converted into chloride either by dissolving it in nitric acid and adding hydrochloric acid, or by heating in chlorine gas. Experiments of this kind by a number of chemists, among whom Stas is conspicuous, have shown that 100 parts of silver combine with 32·8418 parts of chlorine. It has also

been shown that 100 parts of silver dissolved in nitric require for exact precipitation 69·1032 parts of chloride of potassium. Now, these 69·1032 parts of potassium chloride must contain 32·8418 parts of chlorine (which is the amount required to combine with 100 parts of silver) and 36·2614 parts of potassium. Then, since 69·1032 parts of potassium chloride correspond to 100 parts of silver,

$$KCl : Ag :: 74{\cdot}4217 : x,$$

and x is the combining ratio of silver = 107·696.

When the value already adopted for oxygen, namely, 15·88, is taken, the combining value for silver deduced from all the best experiments is 107·13. By similar calculations the number for potassium is 38·82, and for chlorine 35·18.

Such numbers as these express, with the greatest approach to accuracy at present possible, the proportion in which these elements enter into certain of their most stable and definite compounds, but the question whether they represent the *atomic* weight, that is, the *smallest* proportions in which the several elements enter into combination, can only be answered by appeal to other considerations. The determination of the atomic weight, then, is accomplished by first estimating as exactly as possible the combining proportion of the element concerned, and then finding, by the application of the methods now to be described, a factor by which this value is to be multiplied or divided. In those cases in which it is possible to apply several of the following rules, it is found that the number indicated by the application of one of them is identical with the number indicated by the others. This is important as showing that when the atomic weights of two elements have been determined by two different methods, the probability that they are comparable with each other and with the same standard amounts to practical certainty. Thus, the atomic weight of silver determined by the specific heat method is equally probable with that of carbon derived from the composition and density of its

vaporisable compounds, although silver forms no volatile compound, and carbon exhibits anomalies in its specific heat.

The atomic weight, as deduced from other considerations, is represented in some cases by the same number as the density of the element in the gaseous state, the density of hydrogen being taken as the unit. This is true of oxygen, nitrogen, chlorine, bromine, iodine, sulphur, selenion, and probably potassium and sodium. But the densities of the vapours of mercury, cadmium, and zinc, as compared with hydrogen, are respectively half the atomic weights, whilst the vapour-densities of arsenic and phosphorus are represented by numbers which are twice the atomic weights. Hence the vapour-density of an element is no guide to the determination of the atomic weight.

I. *Application of the Law of Avogadro.*—According to the system here adopted, and which will be further dwelt upon in the next chapter, the bulk of one part by weight of hydrogen is regarded as the volume of the atom of that element, and is selected as the unit for comparison of other volumes, atomic and molecular. Twice this bulk of hydrogen contains a molecule, and all molecules in the gaseous state occupy the same volume. Now, according to the atomic theory, a molecule cannot contain less than one atom of any element; and, consequently, if we ascertain what is the smallest quantity of an element contained in a molecule of any compound of which it may be a constituent, we shall have determined the atomic weight of the element.

The atomic weight, then, may be said to be the smallest weight of the element ever found in two volumes of the vapour of any of its volatile compounds, the bulk of one part by weight of hydrogen, at the same temperature and pressure, being considered as one volume.

Suppose, for example, it is required to find by this rule the atomic weight of oxygen, we have only to ascertain the vapour densities of a number of compounds containing that

element, and the weight of oxygen contained in each. The results are then tabulated in the following manner:—

Volatile Compounds containing Oxygen.	Relative Density, that is Weight of 1 Volume of Gas or Vapour at same Temp. and Pressure.	Weight of Two Volumes.	Weight of Oxygen contained in Two Volumes.
Water	9	18	16
Carbon monoxide	14	28	16
Carbon dioxide	22	44	32
Sulphur dioxide	32	64	32
Sulphur trioxide	40	80	48
Nitrous oxide	22	44	16
Nitric oxide	15	30	16
Alcohol	23	46	16
Ether	37	74	16
Acetic acid	30	60	32
&c.	&c.		&c.

Two volumes of the vapour of any volatile compound, therefore, never contain less than 16 parts of oxygen, and hence 16, or more accurately 15·88, is accepted as its atomic weight.

This is a rule of very general applicability, for although a great many of the elements, carbon for example, are quite incapable of being volatilised at any manageable temperature, they yield a large number of easily volatile compounds.

There are, however, many metals which are neither vaporisable by themselves nor when in union with other elements. In such cases this rule cannot be applied, and information has to be sought in a different direction.

II. *Law of Dulong and Petit.*—'The specific heats of the solid elements are inversely proportional to their atomic weights.' Whence it follows that the product of the multiplication of the specific heat by the atomic weight is a constant number.

In the following table are given the specific heats of the most important of the elements, together with their atomic weights:—

Name of the Element.	Atomic Weight.	Sp. Ht. of Equal Weights.	Sp. Ht. of Atomic Weights.
Aluminium	27	·2143	5·78
Antimony	120	·0508	6·09
Arsenic	75	·0814	6·11
Bismuth	208	·0308	6·40
Boron (crystallised)	11	·2300	2·53
Bromine (solid)	80	·0843	6·74
Cadmium	112	·0567	6·35
Carbon	12	—	—
α. Wood charcoal	—	·2410	2·89
β. Natural graphite	—	·2020	2·42
γ. Diamond	—	·1469	1·76
Cobalt	59	·1030	6·07
Copper	63·5	·0952	6·04
Gold	197	·0324	6·36
Iodine	127	·0541	6·87
Iron	56	·1138	6·37
Lead	207	·0314	6·50
Lithium	7	·9408	6·58
Magnesium	24·3	·2499	6·07
Mercury (solid)	200	·0319	6·38
Nickel	58·7	·1092	6·41
Phosphorus	31	—	—
α. Common	—	·1895	5·87
β. Red	—	·1698	5·26
Platinum	195	·0324	6·31
Potassium	39	·1655	6·54
Silicon	28	—	—
α. Graphitoidal	—	·1810	5·07
β. Crystallised	—	·1650	4·62
γ. Fused	—	·1380	3·86
Silver	108	·0570	6·16
Sodium	23	·2934	6·75
Sulphur (octahedral)	32	·1776	5·68
Tin	119	·0562	6·69
Zinc	65	·0956	6·23

The greater number of the specific heats given in this table were determined by Regnault. A glance down the fourth column will show that, with three exceptions (boron, carbon, and silicon), the amount of heat required to produce the same change of temperature in the different elements is nearly the same in all cases when the quantities operated upon are in the proportion of their atomic weights. That the numbers representing the atomic heats are not

found to be exactly identical is due partly to unavoidable errors in the estimation of the specific heats, and partly to the fact that the different elements are not dealt with under conditions which are strictly comparable with one another. Thus, solid mercury and solid bromine, at the temperatures at which the specific heats were determined, are much nearer to their melting points than are the solids, copper and iron, at the temperatures at which the same operation was performed upon them. The presence of impurities in the material used for experiment and other circumstances, such as the assumption of different allotropic forms by some of the elements, tend to the introduction of further uncertainty.

Experiments made by F. Weber in 1876 prove that the specific heats of the three exceptional non-metallic elements, carbon, silicon, and boron, increase rapidly with the temperature, and become nearly constant at high temperatures. At 600°, or a little above, the number found for diamond was ·4589, and that for graphite ·4670. These numbers multiplied by 12 give 5·5 and 5·6 respectively as the atomic heat of carbon in these two forms. It will be observed that these numbers are not appreciably lower than those assigned to several other elements of small atomic weights. Increase of specific heat as the temperature rises is, however, not confined to the exceptional instances mentioned, for several metals such as nickel and cobalt, and especially aluminium, show considerable increase. The true specific heat of aluminium at about −180°C. is ·122, at about 20° it is ·205, and at 400–450° it is ·253; the corresponding atomic heats are 3·3, 5·5, and 6·8. In this case, then, in passing from a low to a high temperature the specific heat is more than doubled. And it appears to be generally true that the specific heats of solid bodies increase as the temperature is raised, though in some cases, silver, tellurium, and platinum for example, the rate of increase is very slow. The original expression of Dulong and Petit is therefore too rigid and should be modified somewhat as follows: 'the

mean specific heats of the solid elements between the temperatures of 0° and 100° C., with the exception of glucinum, boron, carbon and silicon, are inversely as their atomic weights.'

If the specific heats of all are determined at such temperatures that they are approaching a maximum, no uniformity is observed, the value of the product of multiplying specific heat by atomic weight varying between 5·5 and 7·9. The simpler rule as stated above acknowledges the existence of exceptional elements, the atomic weights of which can be determined by appeal to other considerations.

The determination of specific heats being always attended by many sources of error, whilst the combining proportion can be fixed with a very considerable degree of accuracy, the application of this rule, like the first, consists essentially in enabling us to decide as to what multiple of the combining proportion is to be taken as the atomic weight. In doing this we are guided by the formula

$$\text{At. Wt.} = \frac{6{\cdot}2}{\text{Sp. Ht.}},$$

where 6·2 is the average atomic heat of a solid element.

Suppose, for example, it is found that 29·75 parts of tin are equivalent to 1 part of hydrogen, and we require to find the atomic weight. The specific heat of tin is ·0562, therefore

$$\text{At. Wt.} = \frac{6{\cdot}2}{{\cdot}0562} = 110{\cdot}3.$$

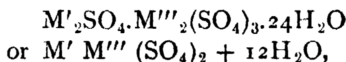
The atomic weight of tin is, however, not taken to be 110·3, but rather such a multiple of 29·75 as comes nearest to that number, and this is found to be 29·75 × 4 or 119.

III. *Isomorphism.*—If a crystal of common potash alum is immersed in a saturated solution of the purple chrome alum, the purple salt is deposited uniformly over the colourless nucleus, so that the crystal increases in bulk though it undergoes no alteration of form. The resulting crystal may

be transferred to a solution of ammonia alum or of iron alum, or manganese alum, and during every fresh immersion it receives a deposit of a different salt upon its surface, the crystalline form, that of the regular octahedron, being throughout preserved.

If instead of thus causing successive layers of the various alums to be superposed one upon the other, solutions of any two of these salts are mixed together, crystals of the same form are deposited containing the elements of both salts.

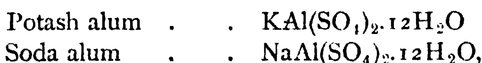
The alums are double sulphates, all containing the same amount of water of crystallisation, and having a composition which may be represented by the general formula



$$M'_2SO_4.M'''_2(SO_4)_3.24H_2O$$
$$\text{or } M'\ M'''\ (SO_4)_2 + 12H_2O,$$

in which M′ may be Cs, Rb, K, Na, Am, Tl or Ag, and M‴ may be Fe, Mn, Cr, Al, Ga, or In.

If, therefore, any two of these compounds are compared together, as, for example,

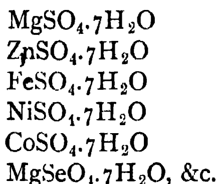


Potash alum . .	$KAl(SO_4)_2.12H_2O$
Soda alum . .	$NaAl(SO_4)_2.12H_2O$,

it is obvious that atom for atom they have the same constitution, but the one contains potassium, the other sodium. This exchange of an atom of one element for an atom of another is in this case effected without producing any alteration in the crystalline structure of the resulting salt, and when bodies thus agree in chemical constitution, and in crystalline form, they are said to be *isomorphous*.

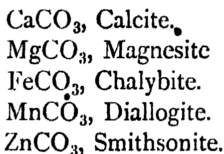
Similar relations are exhibited in the following groups of salts, from which it will be seen that elements which resemble one another in chemical characters are frequently capable of mutual replacement without effect on the crystalline form of the compounds into which they enter.

Magnesium Group of Sulphates and Selenates.



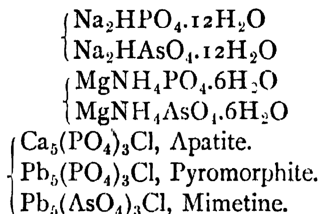
$MgSO_4.7H_2O$
$ZnSO_4.7H_2O$
$FeSO_4.7H_2O$
$NiSO_4.7H_2O$
$CoSO_4.7H_2O$
$MgSeO_4.7H_2O$, &c.

Minerals Isomorphous with Calcite.



$CaCO_3$, Calcite.
$MgCO_3$, Magnesite
$FeCO_3$, Chalybite.
$MnCO_3$, Diallogite.
$ZnCO_3$, Smithsonite.

Phosphates and Arsenates.



$\begin{cases} Na_2HPO_4.12H_2O \\ Na_2HAsO_4.12H_2O \end{cases}$

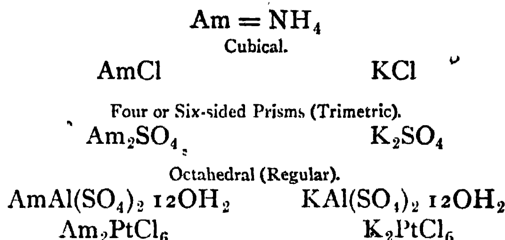
$\begin{cases} MgNH_4PO_4.6H_2O \\ MgNH_4AsO_4.6H_2O \end{cases}$

$\begin{cases} Ca_5(PO_4)_3Cl, \text{ Apatite.} \\ Pb_5(PO_4)_3Cl, \text{ Pyromorphite.} \\ Pb_5(AsO_4)_3Cl, \text{ Mimetine.} \end{cases}$

From these and many other instances of the same kind chemists have been led to infer that when two bodies, composed of the same or similar elements, crystallise in forms belonging to the same crystallographic system, they generally contain the same number of atoms united together in a similar manner.

This statement must be considered to include cases in which groups of atoms (compound radicles) take the place and perform the part of single elementary atoms. The compounds of ammonia with acids, for example, are isomorphous with the corresponding salts of potassium, and

a constitution is therefore attributed to the ammoniacal salts similar to that of the potassic salts, the symbols NH_4 being the representative of the metal in these compounds. Thus in the following pairs of compounds there is the most complete concordance in chemical characters as well as in crystalline form.



$$Am = NH_4$$

Cubical.

$AmCl$	KCl

Four or Six-sided Prisms (Trimetric).

Am_2SO_4	K_2SO_4

Octahedral (Regular).

$AmAl(SO_4)_2\ 12OH_2$	$KAl(SO_4)_2\ 12OH_2$
Am_2PtCl_6	K_2PtCl_6

Although some of the relations between external crystalline form and chemical constitution are still involved in obscurity, the existence of a great number of well-marked cases of isomorphism is a fact which is familiar to every chemist, and occasionally the application of this principle has led to the settlement of questions relating to atomic weights, regarding which there had been previously more or less of uncertainty.

For instance, alumina, the only known oxide of aluminium, is believed to have the same constitution as ferric oxide, because not only do the oxides themselves agree in crystalline form, but they are capable of replacing each other in their compounds without disturbing the crystalline structure of these bodies. Now, since ferric oxide is universally regarded as a sesquioxide, that is, containing in each molecule two atoms of the metal to three atoms of oxygen, alumina is believed to be formed upon the same type, and if the formula Fe_2O_3 be employed to represent ferric oxide, Al_2O_3 must be admitted as the formula for alumina. If these considerations have to be applied to the determination of the atomic weight of the metal, we have

only to refer to the analysis of alumina to find that 100 parts contain

52·94 parts of aluminium,
and 47·06 " " oxygen.

And since, according to the formula, we have 3 × 16 or 48 parts of oxygen united with $2x$ parts of metal, we can easily calculate the value of x (= 27), which is the atomic weight.

The following is another interesting example :—

It is well known that the crystalline forms of sodium nitrate and calc-spar are nearly identical, and a crystal of calc-spar immersed in a saturated solution of the nitrate will grow by uniform deposition of that salt all over its surface. Arragonite (another form of calcium carbonate) is also found in prisms of the same form as common potassium nitrate. These facts tend to prove that calcium carbonate probably contains the same number of atoms as the nitrates of potassium and sodium, and that its formula should be

$CaCO_3$
if the others are KNO_3
and $NaNO_3$ respectively.

But this formula cannot be used unless we assume that the atomic weight of calcium is 40, a number which agrees with the value deduced from other considerations.

IV. *Chemical Evidence.*—But independently of the existence of vaporisable compounds and of any application of Avogadro's hypothesis, the atomic weight may in some cases be determined by appeal to purely chemical considerations. Take the case of oxygen again. We know by analysis that 100 parts of water contain 88·88 parts of oxygen to 11·11 parts of hydrogen. These proportions might be expressed by the formula HO (if O = 8), or by H_2O (if O = 16), or by H_3O (if O = 24). To decide between these several values we note the results of decomposing water by chemical agents. Potassium acting upon

water produces caustic potash, which contains all the oxygen together with *half* the hydrogen of the water.

In this decomposition, then, the hydrogen is displaced in two equal portions, and no reaction is known in which the hydrogen of water is divisible into more than two parts. The oxygen, on the other hand, may be displaced by chlorine, but no such division occurs in this case, and no compound is known in which the whole of the hydrogen in water is associated with half the oxygen and a quantity of chlorine equivalent to the other half. There is no compound intermediate between hydrogen chloride and water.

These facts are expressed in the formula H_2O, where the atomic weight of oxygen is assumed to be 16 (approximately), and the atomic weight of hydrogen is 1. The same value for the atomic weight of oxygen must be admitted in the formulæ for ether and for the anhydrides of monobasic acids, like acetic acid. According to views prevailing up to about 1860, alcohol was hydrated oxide of ethyl,[1] EtO.HO, and acetic acid was hydrated oxide of acetyl,[2] AcO.HO (O being = 8). But the conversion of alcohol into ether, and acetic acid into its anhydride, cannot be effected by withdrawing the elements of water. In the operations by which these transformations are effected an intermediate compound is always formed, which represents a second molecule of the alcohol or acid. Thus, ether may be produced from alcohol by first displacing from it an atom of hydrogen by potassium, as in the case of water, producing the compound EtOKO, and this is converted into ether by making it react with the chloride or iodide of ethyl, EtCl or EtI. So that the resulting ether is EtOEtO.

The series of compounds thus produced is best represented as parallel with the series formed from water, adopting in both cases and for similar reasons the assumption

[1] Et = C_4H_5, if C is 6.

[2] Ac = $C_4H_3O_2$, if C is 6, and O is 8.

that each molecule contains one atom and not two atoms of oxygen.

Water, HHO.	Alcohol, EtHO.
Potassium hydroxide, KHO.	Potassium ethoxide, KEtO.
Potassium oxide, K_2O.	Ethyl oxide, Et_2O.

Again, acetic acid can be deprived of the elements of water only with the greatest difficulty, even by the action of so powerful a dehydrating agent as phosphorus pentoxide; but the anhydride, formerly called anhydrous acetic acid, is instantly produced when acetyl chloride is mixed with acetic acid or a dry acetate. So that the constitution of these compounds is similar to that of the ethyl series just described, thus :—

Acetyl chloride, AcCl.
Acetic acid, AcHO.
Potassium acetate, KAcO.
Acetic anhydride, Ac_2O.

In all these cases the value for the atomic weight of oxygen is necessarily 16 (approx.).

The valuation of the atomic weight of carbon may be effected in a somewhat similar manner. Marsh gas is the simplest compound of carbon and hydrogen known. It contains 3 parts by weight of carbon to 1 part of hydrogen, and assuming the value 3 for the symbol C, this composition could be expressed by the formula CH. By the same hypothesis the formula of carbon perchloride is CCl. But when chlorine acts upon marsh gas it forms three intermediate products; hence the hydrogen in marsh gas is divisible into four equal parts, and the hydrogen must be present in the form of four atoms, and the formula becomes C_4H_4. If there are four atoms of carbon in a molecule of marsh gas, we must believe that these four are united together to form a group which remains intact

throughout all the vast array of compounds derived from marsh gas, and it would be difficult to assign a reason for the three intermediate stages in the chlorination of marsh gas. So that, since there is no evidence of the divisibility of the carbon in the two oxides of carbon, in marsh gas, in chloroform, and other allied substances, one molecule of each of these compounds is represented as containing one atom of carbon, to which the proportional value 12 is given.

It is evident, therefore, that the valuation of atomic weights by chemical methods also involves the determination of the relative molecular weights of a number of compounds. A more direct consideration of this part of the subject is contained in the next chapter.

CHAPTER VI.

MOLECULAR WEIGHTS AND FORMULÆ.

WHEN a compound has been analysed, it is usual in the first instance to represent its composition by the percentages of the several elements of which it is made up. Acetic acid, for example, contains—

Carbon	40·0
Hydrogen	6·6
Oxygen	53·4

in 100 parts. The next step is to endeavour to write a formula which, while expressing the same facts more compactly, gives, at the same time, the number of atoms of the constituent elements, and fixes the relative weight of the molecule.

If the atomic weights of the elements were all equal, the formula would be a mere repetition of the percentages; but since they are different, the number of atoms of the several elements contained in equal weights must be inversely as their atomic weights.

The simplest rule for deducing the formula of a compound from its percentage composition is, therefore, to divide the respective quantities by the atomic weights of the elements.

Thus, if we divide the percentages of carbon, hydrogen, and oxygen in acetic acid by the atomic weights of carbon, hydrogen, and oxygen respectively, we arrive at these results.[1]

$$\frac{40}{12} \quad . \quad . \quad . \quad . \quad . \quad = 3{\cdot}3$$

$$\frac{6{\cdot}6}{1} \quad . \quad . \quad . \quad . \quad . \quad = 6{\cdot}6$$

$$\frac{53{\cdot}4}{16} \quad . \quad . \quad . \quad . \quad . \quad = 3{\cdot}3$$

So that evidently there are as many atoms of oxygen present as there are of carbon, and there are twice as many hydrogen atoms. The simplest formula, then, that can be written for acetic acid is CH_2O; but whether this is to be taken as representing a molecule of acetic acid or whether the true formula is some multiple of this, such as $C_2H_4O_2$ or $C_3H_6O_3$, remains to be decided by considerations which now require to be examined.

VAPOUR DENSITY AND MOLECULAR WEIGHT.

According to the law of Avogadro, equal volumes of all true gases, irrespective of chemical composition, contain under the same conditions of temperature and pressure the same number of molecules. It follows from this that

[1] See also Examples and Exercises, No. 90.

the weights of equal volumes must be proportional to the weights of the molecules of which the gases are composed.

This is the principle of the only *direct* method for ascertaining the relative weights of these molecules.

Comparing together, for example, equal measures of hydrogen and hydrogen chloride gases, we find their respective weights represented by the numbers 1 and 18·25. But the weight of hydrogen contained in hydrogen chloride is exactly half the weight of the same element contained in an equal measure of hydrogen, and if we assume that there is one atom of hydrogen in a molecule of hydrogen chloride (and by the theory there cannot be less than one atom), we arrive at the conclusion that the molecule of hydrogen consists of at least two atoms. But, further, we have every reason to believe that while the molecule of hydrogen chloride contains at least one atom of hydrogen, it does not contain more than one atom. When metals act upon hydrogen chloride the hydrogen is expelled all at once, and not in several portions, as in the case of water and ammonia. So that, assuming the atomic weight of hydrogen as 1 unit of weight, the molecule of hydrogen chloride must weigh 36·5 units. The weight of hydrogen equal in bulk to this, that is to say, one molecule of hydrogen or two unit volumes, must accordingly be 2.[1]

[1] The student will now perceive why 2 volumes and not 1 volume or 3 or 4 volumes is regarded as the standard volume of molecules. One volume would be inconvenient, because we find that the molecule of hydrogen can be divided into two equal parts, and this would necessitate the use of fractions. Three volumes would be incorrect, because the hydrogen molecule is divisible into two and not into three atoms. Four volumes would also be inadmissible, because the same bulk, that is one molecule of hydrogen chloride, would then be represented as containing two atoms of hydrogen and two atoms of chlorine, H_2Cl_2. Whereas it is a matter of fact that neither the hydrogen nor the chlorine in hydrogen chloride is divisible into separate parts.

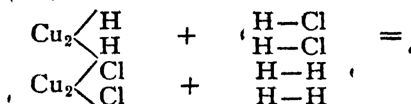
The same conclusions may be established by a slightly different form of the same argument. Equal volumes of hydrogen and chlorine react to form hydrogen chloride equal in volume to the mixture, or twice the volume of the hydrogen or of the chlorine alone. So that whatever is the number of molecules in the hydrogen gas employed, the matter composing them is distributed into twice the number of molecules of hydrochloric acid. And as there is every reason for supposing that the hydrogen chloride molecules are all exactly alike, each of the original hydrogen molecules is broken up into two equal and similar portions.

Again, two volumes of hydrogen mixed with one volume of oxygen, at any temperature above the boiling-point of water, make three volumes of the mixed gas. If a spark be now passed into the mixture the gases ignite, and on cooling to the original temperature leave two volumes of steam—that is, a quantity double the bulk of the oxygen used. Here again the matter composing the oxygen molecules is distributed into twice as many molecules of steam, and hence each of the oxygen molecules must have been divisible into two equal and similar parts.

Regarding the diatomic character of hydrogen and oxygen molecules, other evidence, independent of any hypothesis concerning the physical constitution of gases, is supplied by the following facts.

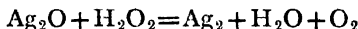
Metallic copper is capable of expelling hydrogen from hydrochloric acid only very slowly, even when boiled with it. But by adding hypophosphorous acid to a warm solution of sulphate of copper, a brown precipitate of cuprous hydride is thrown down, and this compound, in contact with hydrochloric acid, evolves hydrogen freely and forms cuprous chloride. This reaction can only be explained upon the assumption that it is *the attraction of the hydrogen in the copper hydride for the hydrogen in the acid*, superadded

to that of the copper for the chlorine, which determines the metathesis :



$$Cu_2 \begin{matrix} H \\ H \end{matrix} + \begin{matrix} H-Cl \\ H-Cl \end{matrix} = Cu_2 \begin{matrix} Cl \\ Cl \end{matrix} + \begin{matrix} H-H \\ H-H \end{matrix}$$

A great many reactions of a similar character are known, chiefly among compounds containing a relatively large proportion of oxygen, part of which escapes in the gaseous form. Thus, when silver oxide is placed in contact with peroxide of hydrogen, the silver is reduced to the metallic state, water is formed, and oxygen gas evolved.



$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2$$

In like manner, permanganic and chromic acids are decomposed by peroxide of hydrogen with evolution of oxygen gas ; and in these and similar reactions it has been proved experimentally that half the oxygen comes from the peroxide, half from the acid or other body with which it is in contact. The conclusion seems inevitable that these two halves of the oxygen had an attraction for each other which was sufficient to upset the equilibrium of the unstable compounds of which they previously formed a part.

It is also well known that substances in the *nascent* state—that is, at the instant of their liberation from compounds—are capable of acting far more energetically than when they are employed in the bodily form. Hydrogen *gas*, for example, is generally incapable of combining with other bodies unless heated or under pressure ; but when materials such as zinc and dilute sulphuric acid, which are capable of yielding hydrogen, are employed, many decompositions and combinations may be brought about which would be otherwise impossible. Solution of sulphur dioxide may in this way be converted into hydrogen sulphide and water by the action of zinc and diluted hydrochloric acid, the

nascent hydrogen attacking and combining with both the sulphur and the oxygen. An instructive experiment, illustrating the power of both nascent oxygen and hydrogen, consists in electrolysing a solution of hydrochloric acid coloured with indigo. The liquid in the neighbourhood of both poles is bleached; at the negative, because the hydrogen there liberated combines with the indigo and forms a colourless compound; at the positive, because the chlorine, acting on the water, disengages oxygen, which, while still nascent, combines with the elements of the indigo, producing a pale yellow substance. Neither oxygen nor hydrogen in the ordinary gaseous form is capable of producing these effects, which are usually supposed to be due to the superior activity of the atoms while still in the free state and before they have partly expended their energies by coupling in pairs; but it must be pointed out that other explanations have been given of the so-called nascent state, which, however, cannot be discussed in this place.

In order, therefore, to express the molecular weights of gases, we must double the numbers representing their relative densities; and this rule is applied to all gaseous and volatile bodies, with the few exceptions referred to in a later chapter.

The application of this principle to those of the elements that are volatile leads to the conclusion that many of them, like hydrogen and oxygen, consist of molecules having a duplex structure, though examples are not wanting of a more complex as well as of a simpler constitution. We come, in fact, to the following classi-fication :—

	Relative Density	Molecular Weight	Molecular Formula
Monatomic Molecules :—			
Mercury	100	200	Hg
Cadmium	56	112	Cd
Zinc	32·5	65	Zn
Iodine (above 1600°)	63·5	127	I

	Relative Density	Molecular Weight	Molecular Formula
Diatomic Molecules :—			
Hydrogen	1	2	H_2
Oxygen	16	32	O_2
Nitrogen	14	28	N_2
Chlorine	35·5	71	Cl_2
Bromine	80	160	Br_2
Iodine (below 500°)	127	254	I_2
Potassium	39	78	K_2
Sulphur (at 900°)	32	64	S_2
Triatomic Molecule :—			
Ozone	24	48	O_3
Tetratomic Molecules :—			
Phosphorus	62	124	P_4
Arsenic	150	300	As_4
Hexatomic Molecule :—			
Sulphur (at 500°)	96	192	S_6

It may be noticed in the table just given that several elements are capable of existing in the gaseous state in the form of molecules of various degrees of complexity. Thus, while vapour of sulphur at temperatures not much above the boiling point of the liquid consists of hexatomic molecules, at higher temperatures these are broken up into groups each containing only two atoms. Many compounds undergo a corresponding simplification when heated, and generally it may be stated that even in the gaseous state the number of atoms which remain united to form a molecule is less at high than at low temperatures. This will be referred to in greater detail in the chapter on 'Dissociation.'

PROPERTIES OF SOLUTIONS IN RELATION TO MOLECULAR WEIGHT.

When a substance is dissolved in a liquid, the freezing point of the solution is lower than that of the pure solvent,

while the boiling point is usually higher. And it has been shown that the effect produced by a given substance is directly proportional to the weight of substance dissolved in a constant quantity of the solvent. Further, it has been found, chiefly through the researches of Raoult, that using the same solvent the freezing point is depressed to the same extent by different substances when used in the proportion of their molecular weights. A corresponding rule applies to the vapour pressure. Upon these facts are based two methods for the estimation of molecular weights, chiefly among organic substances, which have come into extensive use within the last few years on account of their applicability to those cases in which the vapour density method cannot be employed (see Chap. on 'Solution').

METHOD I. *based on observation of the freezing point of a solution.*

A solution of the compound is prepared containing a known quantity of the substance in 100 grams of the liquid, and the strength is so adjusted that the freezing point of the latter shall not be reduced more than about 1° to 2°. Let P be the weight in grams of substance in 100 grams of solvent, and C the depression observed, then $\frac{C}{P}$ would be the reduction of freezing point produced by 1 gram, and $\frac{MC}{P}$ the reduction produced by an amount of substance proportional to the molecular weight M, taken in grams. Call this T, then the equation

$$T = \frac{MC}{P} \quad \text{or} \quad M = \frac{TP}{C}$$

affords the means of estimating the molecular weight if T be previously known for the solvent employed. For organic

compounds the following values of T have been determined as constant :—

Water	19
Acetic acid	39
Benzene	49

Attempts have been made to apply the principle of this method to the determination of the molecular weights of metals by observation of their effects on the solidifying point of sodium, tin, and some other metals.

For many acids, bases, and inorganic salts the effect on the freezing point of water is about twice as great as theory would appear to indicate. This effect is believed to be due to ionic dissociation (see Chap. XIX.).

METHOD II. *based on observation of the boiling point or vapour pressure of a solution.*

It has already been stated that the vapour pressure of a volatile liquid is diminished to the same extent by the addition of molecular proportions of different substances soluble in the liquid. This is made the basis of another method of estimating molecular weights, which may take one of two forms. One process consists in determining accurately the boiling point of the pure liquid in a special apparatus, then adding successive weighed portions of the substance and observing the rise of boiling point after each addition. The calculation is made by means of a formula obtained in the same way as for the freezing point. Using the same letters, C now stands for elevation of boiling point, and T for the molecular constant, thus :

$$\frac{CM}{P} = T \qquad \text{or} \qquad M = \frac{TP}{C}$$

The following are values of T for a few liquids :—

Ethyl ether	21·1
Benzene	26·7
Carbon disulphide	23·7
Alcohol	11·5

The other process is based on a comparison of the vapour pressures of the solution and the pure solvent by noting the vaporisation of both in a current of air at the same temperature. The process is carried out by passing the same current of dry air first through bulbs containing the solution of known strength, then through a second set of bulbs containing the solvent, the whole being immersed in a bath of constant temperature. The loss of weight of the bulbs containing the solution being proportional to the vapour pressure of the solution, and the loss of weight of the pure solvent being proportional to the difference between the vapour pressures of the solution and the pure solvent, then if the strength of the solution is known the data for estimating the molecular weight are obtained. Let m be the molecular weight of the solvent, p the number of grams of dissolved substance in 100 grams of the solvent, s′ the loss of weight of the bulbs containing the solution, s the loss of weight of the solvent, f′ the vapour pressure of the solution, f the vapour pressure of the pure liquid, and M the molecular weight of the substance :—

$$M = m.p. \frac{\cdot 01\ f'}{f - f'}$$

Also

$$\frac{f'}{f - f'} = \frac{s'}{s}$$

Therefore :—

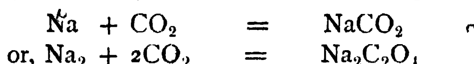
$$M = m.p. \frac{\cdot 01\ s'}{s}$$

SYNTHESIS AND ANALYSIS OF COMPOUNDS.

There are several other sources of information which will help in the solution of the problem of the molecular weights and formulæ of compounds. One very important kind of argument is deduced from a knowledge of the mode or modes in which the compound may be formed,

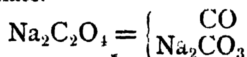
and of the products of its decomposition under the influence of reagents.

For example, oxalate of sodium is formed when carbon dioxide gas is passed over heated sodium. The change might be represented by either of the following equations :—



$$Na + CO_2 = NaCO_2$$
$$\text{or, } Na_2 + 2CO_2 = Na_2C_2O_4$$

But the doubt, if there were any, would be resolved in favour of the latter alternative, by the observation that when sodium oxalate is heated it yields carbonic oxide gas, leaving a residue of carbonate.



$$Na_2C_2O_4 = \begin{cases} CO \\ Na_2CO_3 \end{cases}$$

The most direct and rational explanation of this is, that a molecule of the salt contains two atoms of carbon, as represented by the formula.

Again, succinic acid may be built up from its elements by a succession of processes, which are briefly represented in the following series of equations ; and from them we learn, even if no other evidence were forthcoming, that succinic acid contains at least four atoms of carbon in a molecule, and hence must have the formulæ here assigned to it.

Carbon poles ignited by the electric current in hydrogen gas give rise to acetylene :



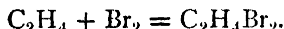
$$C_2 + H_2 = C_2H_2.$$

Acetylene can be made to combine with hydrogen, yielding ethylene, the known density of which gas renders impossible any doubt as to its molecular weight :



$$C_2H_2 + H_2 = C_2H_4.$$

Ethylene combines with bromine thus :



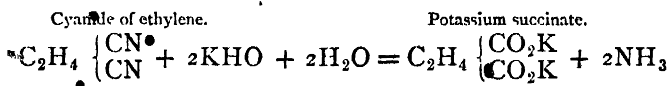
$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

This dibromide may be converted into a cyanide :



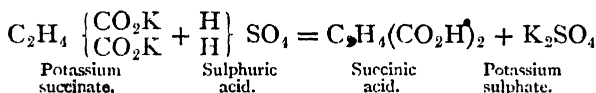
$$C_2H_4Br_2 + 2KCN = C_2H_4C_2N_2 + 2KBr.$$

Lastly, this cyanide, under the influence of boiling alkali, assimilates the elements of water, and yields up its nitrogen in the form of ammonia.



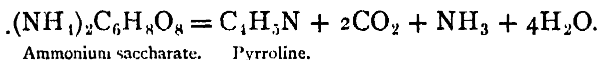
$$C_2H_4 \begin{cases} CN \\ CN \end{cases} + 2KHO + 2H_2O = C_2H_4 \begin{cases} CO_2K \\ CO_2K \end{cases} + 2NH_3$$

From this salt the acid may be procured by the action of sulphuric acid.



$$C_2H_4 \begin{cases} CO_2K \\ CO_2K \end{cases} + \begin{matrix} H \\ H \end{matrix} \Big\} SO_4 = C_2H_4(CO_2H)_2 + K_2SO_4$$

Evidence is also derivable from a study of products of decomposition. Analysis of glucose, for example, gives proportions of carbon, hydrogen, and oxygen, which may be expressed by $(CH_2O)_n$, a formula identical with that of acetic acid, a totally different substance. The problem is to determine the value of n. When glucose is gently oxidised it yields saccharic acid, a well-established dibasic acid, the two potassium salts of which are respectively represented by the formulæ $KC_6H_9O_8$ and $K_2C_6H_8O_8$. Ammonium saccharate when heated splits up according to the following equation :—



$$(NH_4)_2C_6H_8O_8 = C_4H_5N + 2CO_2 + NH_3 + 4H_2O.$$

Further oxidation of saccharic acid yields oxalic acid, $H_2C_2O_4$, and oxalic acid in turn yields carbonic acid.

Hence the molecule of saccharic acid contains C_6, and consequently the molecule of glucose from which it is formed very probably contains at least $C_6H_{12}O_6$, inasmuch as products of oxidation almost always contain either the same number of carbon atoms as the compounds from which they were derived, or a smaller number.

This rule, however, though a very useful guide, is not without exceptions. Thus—

Alcohol, C_2H_6O	. yields	aldehyd, C_2H_4O and acetic acid, $C_2H_4O_2$
α propyl alcohol, C_3H_8O		propionic aldehyd, C_3H_6O and propionic acid, $C_3H_6O_2$
β propylic alcohol, C_3H_8O	,,	acetone, C_3H_6O or acetic acid, $C_2H_4O_2$ and formic acid, CH_2O_2
Toluene, C_7H_8 . .	,,	benzoic acid, $C_7H_6O_2$
Xylene, C_8H_{10} . .	,,	toluic acid, $C_8H_8O_2$ or phthalic acid, $C_8H_6O_4$
&c.		&c.

But—

Benzene, C_6H_6 . .	,,	benzoic acid, $C_7H_6O_2$
Phenol, C_6H_6O . .	,,	first phenoquinone, $C_{18}H_{16}O_4$

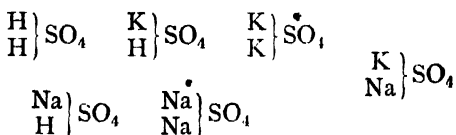
In such cases the condensation results from several molecules being simultaneously attacked.

The compound last named, phenoquinone, is known to possess the formula ascribed to it because it is otherwise produced by the union of one molecule of quinone, $C_6H_4O_2$, with two molecules of phenol, C_6H_6O, no other product being formed at the same time.

SATURATING POWER OF ACIDS AND BASES.

In the examination of acids and bases, and other compounds which are capable of entering into combination readily, or of suffering the replacement of some of their elements by simple reactions which do not involve destruc-

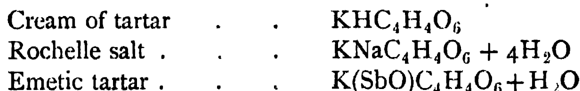
tion of the molecule, the process for determining the molecular weight is generally easy. Suppose, for instance, it is required to determine the molecular weight of sulphuric acid, it is only necessary to add to it various quantities of potash or soda to discover that there are two, and two only, distinct and definite sulphates of potassium and sodium, and that even double salts are possible, in which the two metals figure side by side, in place of the hydrogen of the acid. So that sulphuric acid and its salts are representable by such formulæ as the following:—



$$\left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 \quad \left.\begin{matrix}K\\H\end{matrix}\right\}SO_4 \quad \left.\begin{matrix}K\\K\end{matrix}\right\}SO_4 \quad \left.\begin{matrix}K\\Na\end{matrix}\right\}SO_4$$

$$\left.\begin{matrix}Na\\H\end{matrix}\right\}SO_4 \quad \left.\begin{matrix}Na\\Na\end{matrix}\right\}SO_4$$

Tartaric acid is a case of similar kind. Its molecular formula cannot be less than $C_4H_6O_6$, on account of the existence of the double tartrates, which prove that the acid contains two replaceable basic hydrogen atoms. Thus:

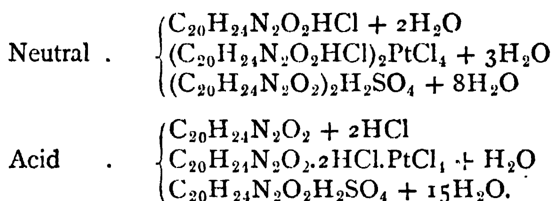


Cream of tartar . .	$KHC_4H_4O_6$
Rochelle salt . . .	$KNaC_4H_4O_6 + 4H_2O$
Emetic tartar . . .	$K(SbO)C_4H_4O_6 + H_2O$

Basic derivatives of ammonia are dealt with in a similar way. If we assume that the molecule of hydrogen chloride is represented by the symbols HCl (= 36·5), the problem is to find what weight of base will enter into combination with 36·5 parts of hydrochloric acid so as to produce a neutral compound. In the case of ammonia itself the compound formed with hydrochloric acid is represented by the formula NH_3HCl, in which NH_3 stands for 17 parts by weight of ammonia. In some cases it is practically more convenient to prepare the double salts which the hydrochloride of ammonia and all similarly constituted compounds form with platinic chloride. Ammonio-chloride

of platinum has the formula $2(NH_3.HCl).PtCl_4$, and that quantity of the basic body which, in this compound, is capable of taking the place of ammonia, NH_3, is generally taken to be its molecular weight.

This principle is applied especially in the case of those natural alkaloids which contain oxygen and are not vaporisable without decomposition. Quinine, from cinchona bark, is an example of the kind. The formula may be either $C_{10}H_{12}NO$ or $C_{20}H_{24}N_2O_2$. The latter is chosen chiefly because quinine forms two classes of salts, namely, neutral compounds, in which $C_{20}H_{24}N_2O_2$ represents the NH_3 in ammonia salts, and acid compounds, containing half the proportion of base or twice the proportion of acid, as in the following formulæ :—



Neutral . $\begin{cases} C_{20}H_{24}N_2O_2HCl + 2H_2O \\ (C_{20}H_{24}N_2O_2HCl)_2PtCl_4 + 3H_2O \\ (C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O \end{cases}$

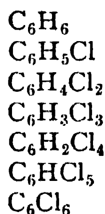
Acid . $\begin{cases} C_{20}H_{24}N_2O_2 + 2HCl \\ C_{20}H_{24}N_2O_2.2HCl.PtCl_4 + H_2O \\ C_{20}H_{24}N_2O_2H_2SO_4 + 15H_2O. \end{cases}$

It appears, therefore, that the number of atoms of nitrogen in the molecule does not determine the saturating power of the base. This is further illustrated by urea, CH_4N_2O, which forms monoacid salts by union with HCl, with HNO_3, or with $\frac{1}{2}H_2SO_4$, &c.; also by such bases as rosaniline, $C_{20}H_{19}N_3$, which combines either with HCl, forming the well-known magenta dye, or with 3HCl, forming a brown crystalline salt.

SUBSTITUTION COMPOUNDS.

In other cases, especially when the compound under examination is neutral, and incapable of entering into combination with other bodies of known molecular weight, the

results of 'substitution' afford information in the direction required. To take an instance, the hydrocarbon benzene is a neutral liquid, neither acid nor basic, which forms no compounds whose constitution throws any light on the question of its molecular weight. It is volatile, and its vapour density would tell all that we require to know, namely, that to represent a molecule of it we must use the formula C_6H_6; but even if we had not this evidence to appeal to, the same result would be indicated by the composition of the products which are formed from it under the agency of chlorine. Acted upon in this way, benzene yields first a product in which one atom of chlorine is combined with six atoms of carbon and five atoms of hydrogen. Now, since this can be shown to consist of one homogeneous chemical compound, and not a mixture, the carbon it contains must be derived from one molecule of benzene, the formula of which therefore becomes C_6H_6. This is confirmed by the succeeding products, the entire series running as follows :—



This removal of hydrogen, and its replacement atom for atom by chlorine or by bromine or iodine, is one of the most remarkable facts in chemistry. For notwithstanding the strong electro-chemical opposition of hydrogen and the halogens, they may be usually exchanged for one another in carbon compounds without altering fundamentally the character of the compound. Acetic acid affords a good instance of this. It yields three chloracetic acids,

which like itself are crystallisable, volatile, monobasic acids.

Name.	Formula.	Melting Point.	Boiling Point.
Acetic acid . . .	$HC_2H_3O_2$	17°	119°
Monochloracetic acid .	$HC_2H_2ClO_2$	62°	186°
Dichloracetic acid . .	$HC_2HCl_2O_2$	– 4°	190°
Trichloracetic acid . .	$HC_2Cl_3O_2$	53°	195°

One other fact often serves as a useful guide in selecting, for carbon compounds especially, a *minimum* formula. Among the vaporisable compounds in which carbon is united with hydrogen alone, or with hydrogen and oxygen, no example is known in which two volumes of the vapour contain an uneven number of atoms of hydrogen. Consequently if the simplest formula deduced from analysis includes such a number it cannot represent the molecular weight, and must be at least doubled. Thus the composition of phthalic acid is expressed exactly by the symbols $C_4H_3O_2$. But according to the present state of knowledge, a molecule of this kind cannot exist; the molecular formula cannot be less than $C_8H_6O_4$. Whether this correctly represents the molecule can only be settled by other inquiries, the general nature of which has already been indicated.

But, notwithstanding the multiplicity of rules which serve to guide chemists in the selection of formulæ whereby to represent molecules, there still remain a large number of bodies which cannot be dealt with by any method at present known. Hence many of the formulæ commonly accepted and employed in chemical works are at best expressions of mere guesses enjoying various degrees of probability. Many difficulties occur, for example, among metallic compounds. The formula CrO_3 is generally used for chromic anhydride, not on account of any direct evidence in favour of it, but because of the existence of a volatile oxychloride, CrO_2Cl_2,

and the analogy of these two compounds with sulphuric anhydride, SO_3, and the corresponding oxychloride, SO_2Cl_2, also on account of the isomorphism of the chromates and sulphates. Again, silicon dioxide is often represented as the analogue of carbon dioxide, but while the latter is undoubtedly represented correctly by the simple formula CO_2, the insolubility, non-volatility, and difficult fusibility of the former render it very probable that the molecular formula is much more complex, perhaps Si_6O_{12}. As, however, no direct evidence exists the expression $nSiO_2$ or Si_nO_{2n} is preferable. So also doubts exist as to the correct mode of representing salts like ferrous and stannous chlorides, there being great probability that the usual formulæ, $FeCl_2$ and $SnCl_2$, should be doubled in order to represent the reacting units or molecules of these compounds.

CHAPTER VII.

VALENCY.

WHEN hydrogen chloride, water, and ammonia are brought into contact, under suitable conditions, with a metal such as sodium, hydrogen is evolved and a compound is formed in which the metal takes the place of the expelled hydrogen. But while in such a process the hydrogen of hydrogen chloride is completely replaced at one operation, the hydrogen of water is divided into two equal parts, and that of ammonia is divided into three. Similarly the hydrogen contained in marsh gas, though incapable of being exchanged for a metal, is divisible into four equal parts by the action of chlorine. On the other hand, the chlorine in hydrogen chloride, the oxygen in water, the nitrogen in ammonia, and the carbon in marsh gas agree in being

indivisible, so that any chemical change which involves removal of any portion of these elements from the four compounds respectively results in the removal of the whole and no intermediate compound can be produced These facts are summed up in the formulæ universally employed for the four compounds referred to, namely, ClH. OH_2, NH_3, CH_4. It is worthy of note that such formulæ may be used as a simple record of these and other facts without reference to theory of any kind.

But as in other cases hypothesis suitable for the explanation of facts is naturally sought for by the mind, and the Atomic Theory supplies what is needed. The formulæ may be taken to mean that one atom of chlorine combines with one atom of hydrogen ; one atom of oxygen with two of hydrogen ; one atom of nitrogen with three of hydrogen ; and one atom of carbon with four of hydrogen, and no compound is known in which one atom of either of these elements—chlorine, oxygen, nitrogen, carbon—is united with a larger quantity of hydrogen than is represented by the formulæ. The student may be again reminded that whereas the atom of chlorine is incapable of retaining more than one atom of hydrogen, the atom of oxygen can hold at the same time two atoms of hydrogen or one atom of hydrogen and one atom of another element, such as potassium.

This difference of combining capacity is recognised in a similar way in other elements, and the following formulæ represent the compounds which some of the more important elements form with hydrogen, and serve to indicate the habitual combining capacity of those elements.

HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si
HI	H_2Se	H_3As	
HF	H_2Te	H_3Sb	

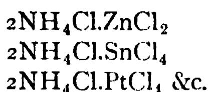
The number which expresses the capacity or habit of com-

bination of a given atom is called its 'valency.' Thus while chlorine and the other halogens are represented as having a valency equal to one unit, the valency of oxygen is usually said to be two, that of nitrogen and phosphorus three, and that of carbon and silicon four in the compounds represented by the formulæ given. To express this in a different way it is convenient to incorporate the Latin numeral and to speak of *univalent*, *bivalent*, *trivalent*, *quadrivalent*, *quinquivalent*, *sexvalent*, or *septivalent* atoms. Or the elements may be referred to as *monad*, *diad*, *triad*, *tetrad*, *pentad*, *hexad*, or *heptad*. The word 'atomicity' was formerly used to indicate the greatest number of atoms of one kind or another with which a given atom is ever found to be united. This term, however, has fallen out of use, and if employed at all is usually applied in reference to the number of atoms presumably constituting the molecule of the element or what might be called its 'atomic density.'

Many facts seem to point to the conclusion that there is no absolute measure of valency. The capacity of saturation of a given atom depends upon the nature of the elements with which it is associated and upon the physical conditions which prevail, especially as to temperature and pressure. An atom of sulphur can take up no more than two atoms of hydrogen, but it is capable of forming a compound with four atoms of chlorine, or with three atoms of oxygen. In like manner, phosphorus forms the compounds PCl_3 and PCl_5, but its affinity for hydrogen extends only to three atoms, PH_3, though a fourth may be taken up if accompanied by an atom of iodine—PH_4I. It has also been observed that the chlorides corresponding with the highest oxides of many of the metals have not yet been produced, and seem to be incapable of existing. Thus there are the oxides CrO_3, UO_3, As_2O_5, Ni_2O_3, but the chlorides Cr_2Cl_6, UCl_5, $AsCl_3$, and $NiCl_2$ indicate the limits of the capacity of these metals for chlorine. It is interesting to notice that in some cases in

which the chloride is missing, the corresponding fluoride is known. For example, the fluorides CrF_6 and AsF_5, the representatives of the unknown chlorides $CrCl_6$ and $AsCl_5$, have been described.

Combining capacity or valency is also to a large extent dependent upon temperature, increasing to an unknown maximum with fall of temperature, diminishing with rise of temperature to a minimum which is reached only when the substance becomes a perfect gas. For example, HCl and NH_3 are both gases which, at 500°, have no apparent action upon each other. On cooling they gradually unite to form solid sal-ammoniac. But even then the affinities of one or more of the elements present are not exhausted, for ammonium chloride unites with other chlorides, forming such compounds as the following:—



$2NH_4Cl.ZnCl_2$
$2NH_4Cl.SnCl_4$
$2NH_4Cl.PtCl_4$ &c.

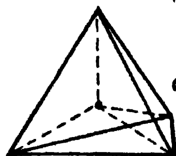
These compounds and sal-ammoniac itself can only exist in the solid state, or perhaps to a limited extent in a state of solution. When heated they yield ammonia and hydrogen chloride gases and other products. The formation of many compounds of this kind leads to the suspicion that the valency of chlorine probably forms the link which binds the other atoms together, and that in the solid state its valency is greater than in its gaseous compounds. The other halogens behave in a similar manner.

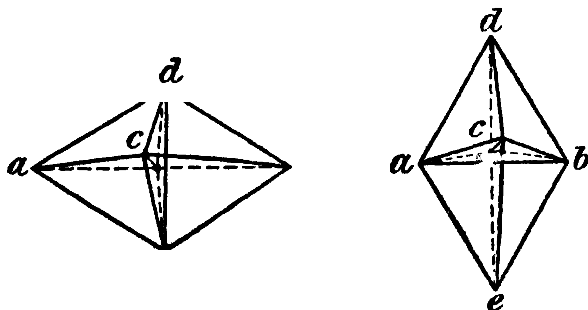
Oxygen, again, is apparently diad or bivalent in water and nearly all other vaporisable compounds containing this element. But in many solid compounds, especially in salts containing water of crystallisation, the facts can best be explained on the hypothesis of a greater combining capacity, probably amounting to four units or more. This question will be discussed in a later chapter.

The variation of valency under varying conditions is analogous to the variation in the number and disposition of the faces of crystals. While every crystallisable substance exhibits a primary or simple form, made up of a minimum number of faces and solid angles, it is usual to find that the form is modified when the conditions in which the crystals are produced are changed. Thus common salt habitually crystallises from water in cubes (6 faces), but from a solution containing urea it yields octahedrons (8 faces). Alum usually forms simple regular octahedrons, but often produces dodecahedrons (12 faces), or forms intermediate between cube or octahedron and dodecahedron. Again, many substances, called on this account *dimorphous*, are capable of assuming two distinct crystalline forms belonging to different crystallographic systems, these different forms being produced most commonly by crystallisation at different temperatures. For example, nitre usually crystallises in six-sided prisms of the trimetric system, but when deposited from a hot solution it often forms rhombohedrons of the hexagonal system. In all cases of this kind the one form is more stable than the other, and there is a constant tendency for the less stable to pass into the more stable form.

Such differences are analogous to the differences in valency manifested in such cases as the ferrous and ferric, stannous and stannic compounds. Valency is now accounted for by certain assumptions regarding the configuration of atoms. Carbon is one of the few elements which has an apparently constant valency, and it was in reference to the element carbon that the idea arose that it might be possible to conceive and to represent the structure of a compound in relation to space of three dimensions. According to this hypothesis the atom of carbon is supposed to consist of a mass, of unknown shape, which is capable of being acted upon or approached by other atoms only in four directions. These are all similar and form with one another the same angles, and thus may be represented

by the lines which join the centre with the solid angles of a regular tetrahedron, as shown in the accompanying figure. The lines joining the centre of the figure with the centre of each face give the same result. Hence it is sometimes represented that the hypothesis supposes the atom to have the form of a regular tetrahedron. This is, however, neither necessary nor justifiable. From observations made quite recently it seems probable that a similar hypothesis is applicable to the cases of lead, tin, and sulphur. With regard to nitrogen, concerning which a similar idea has been adopted, the figure required is somewhat different, for nitrogen has a valency always represented by an odd number, which may be 3 or 5. A hexhedron with equilateral triangle for base, and the remaining two solid angles on opposite sides of the base at a distance either greater or less than the distance from the centre to one of the angles of the base, would provide the requisite conditions. A molecule of a compound of quinquivalent nitrogen would then be formed by attachment of the atoms surrounding the nitrogen in directions indicated by the lines drawn from the centre to the solid angles of the figure; thus:





In compounds which are electrolytes, that is, are decomposed into positive and negative components by the

electric current, the valency of an atom is measured by the number of units of electricity with which it is supposed to be charged. This point will be referred to in a later chapter.

The capacity of combination habitually shown by the commoner elements in their more familiar compounds is shown in the following table :—

VALENCY OF THE PRINCIPAL ELEMENTS.

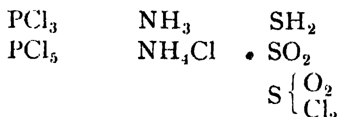
Non-Metals.					
Monads.	Diads.	Triads.	Tetrads.	Pentads.	Hexads.
F	O	B	C	N	S
Cl	S	N	Si	P	
Br		P	S		
I					
Metals and Metalloids.					
Monads.	Diads.	Triads.	Tetrads.	Pentads.	Hexads.
Ag	Hg	Al	Pt	As	
Na	Cu	Cr		Sb	Cr
K	Co Mn	Mn	Sn	Bi	Mn
	Ni Fe	Fe			Fe
	Cd Ba	As	Pb		
	Zn Sr	Sb			
	Mg Ca	Bi			
	Pb				

LAW OF EVEN NUMBERS.

When several compounds are formed by the union of two elements in different proportions, it is very commonly noticed that the change of valency or combining capacity of the central atom to which the rest may be supposed to be attached takes place by pairs of units.

Phosphorus, for example, forms two chlorides; nitrogen combines with three atoms of hydrogen in ammonia, and

with four atoms of hydrogen and an atom of chlorine in chloride of ammonium. Sulphur also yields compounds, in which one atom of that element is combined with two atoms of hydrogen, with two atoms of oxygen, and with two atoms of oxygen and two atoms of chlorine. The formulæ of these compounds are represented as follows :—



$$PCl_3 \qquad NH_3 \qquad SH_2$$
$$PCl_5 \qquad NH_4Cl \qquad SO_2$$
$$S\begin{cases} O_2 \\ Cl_2 \end{cases}$$

It will be observed that the difference in the first case amounts to two atoms of chlorine, which represent two atoms of hydrogen, the unit of valency. In the second case, one atom of hydrogen and one atom of chlorine have been added. In the third, the oxide SO_2 may be taken to represent a hypothetical hydride SH_4, whilst the oxychloride corresponds with the unknown compound SH_6. In each series, the advance in combining power is equivalent to the assumption of two atoms of hydrogen.

It has already been pointed out that compounds of carbon with hydrogen alone, or with hydrogen and oxygen, always contain an even number of atoms of hydrogen, and that an uneven number of atoms of hydrogen can never exist in the molecule of a carbon compound unless it includes at the same time chlorine, nitrogen, or some other element of uneven valency.

It seems, therefore, that, as a general rule, the index of valency of any given atom is either an even or an odd number ; or, as it has been expressed, elements are uniformly either 'artiad' or 'perissad.'[1] And consequently the sum of the indices of valency of all the atoms present is an even number.

But there are not wanting exceptions to these statements ; as shown in the following examples :

[1] ἄρτιος, even, and περισσός, odd.

Nitric Oxide.—This most remarkable compound is a colourless gas, difficult to liquefy, almost insoluble in water, and unchanged by heat. It exhibits all the characteristics of an unsaturated compound. Thus it unites with oxygen, with chlorine, with sulphur trioxide, and with many metallic salts.

It is composed of 14 parts of nitrogen with 16 parts of oxygen; its relative density is 15 ($H=1$), and consequently its molecular weight is 30. It therefore contains one atom of nitrogen (perissad), combined with one atom of oxygen (artiad), and thus it breaks the law of even numbers. This difficulty might be avoided by employing the double formula, N_2O_2, but that its low density and difficult condensability point conclusively to the simpler expression NO as the symbol of its molecule.

Nitric Peroxide.—This compound is described in the Chapter on Dissociation. At 150°–200° the density of the gas is 23 times that of hydrogen at the same temperature. Whence the molecular weight is 46, and the formula NO_2 represents a molecule. Even at much lower temperatures this compound exists mixed with the tetroxide, N_2O_4. In this case also it is obvious that so long as nitrogen is supposed to be perissad while oxygen is artiad, free or unemployed valency of either the nitrogen or the oxygen must be assumed.

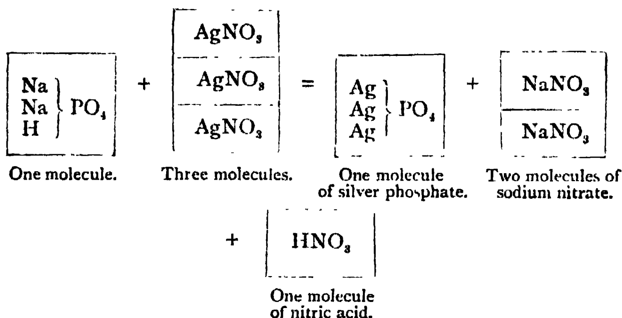
Tungsten and Molybdenum Pentachlorides, WCl_5 and $MoCl_5$.—These compounds afford very remarkable instances of the association of an artiad atom with an uneven number of perissad atoms, and consequent infraction of the law under discussion. Hexchlorides of both these elements corresponding with their trioxides, exist; but these chlorides when heated are split up into pentachlorides and free chlorine. The pentachlorides are volatile without decomposition, and the vapours exhibit normal densities.

COMPOUND RADICLES.

Any portion of a molecule which is capable of being detached and transferred to some other molecule is called a

'radicle,' whether it consists of a single atom or of a group of atoms. The term 'compound radicle' is, however, not usually applied to a group unless it makes its appearance in several different bodies. Compound radicles present different degrees of valency, just as do the atoms of which they are built up, so that they are capable of linking together various proportions of other elementary or compound radicles. This fact may be experimentally verified by such reactions as the following:—

Ordinary disodic phosphate is alkaline to test-paper; silver nitrate is neutral. When these two salts are mixed together in equivalent proportions a yellow precipitate of phosphate of silver is thrown down, whilst the liquid becomes strongly acid. The reason of this is apparent when we express the metathesis in the form of an equation.



The group PO_4 is trivalent, and so it holds together the two atoms of sodium and one atom of hydrogen in one molecule. But when the interchange occurs, these become respectively united with three (NO_3) groups, each of which is univalent, and incapable of connecting itself with more than one atom at a time. Three new molecules result, one of which is nitric acid, the presence of which can be recognised by test-papers.

Although nearly all unsaturated compounds are capable

of entering into combination, and many of them perform the part of well-defined radicles, it does not follow that all radicles should be capable of isolation, and the definition of a radicle by no means involves this idea. On the contrary, we have already examined phenomena (pp. 85 to 87) which indicate that when atoms such as H, Cl, O, or N are liberated from combination, they combine in pairs, and thus satisfy each other's attractions, unless they find themselves in the presence of other radicles with which they can immediately unite. Compound radicles resemble elementary atoms in this respect. None of the following groups, for example, are known in the free state, the formulæ [1] representing semimolecules, or what may be termed chemical atoms of these radicles.

Hydroxyl $(OH)'$ contained in acids, alcohols, and metallic hydroxides.
Potassoxyl $(OK)'$ contained in potassium oxysalts.
Cyanogen $(CN)'$ contained in cyanides.
Ammonium $(NH_4)'$ contained in the salts of ammonia.
Arsendimethyl $\left(As\begin{matrix}CH_3\\CH_3\end{matrix}\right)'$ in kakodyl and its compounds.
Methyl $(CH_3)'$ in methylic alcohol and derivatives.
Amidogen $(NH_2)'$ in primary amines and amides.
Methenyl $(CH)'''$ in chloroform and similar bodies.

When displaced from any of their compounds they do not remain isolated, but unite in pairs, producing molecules which in some cases are stable enough to maintain an independent existence.

We have, for example—

Radicle Name.		Corporate Name.
Hydroxyl	.	Hydrogen Dioxide $(OH)_2$ or O_2H_2
Potassoxyl	.	Potassium Dioxide $(OK)_2$ or O_2K_2
Cyanogen	.	Cyanogen Gas $(CN)_2$ or C_2N_2

[1] The dashes serve to indicate the usual valency of each group.

Radicle Name.	Corporate Name.	
Arsendimethyl	Kakodyl	$\left(As\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2$ or $As_2(CH_3)_4$
Methyl .	Ethane	$(CH_3)_2$ or C_2H_6
Amidogen	Diamidogen or Hydrazine	$(NH_2)_2$ or N_2H_4
Methenyl .	Acetylene	$(CH)_2$ or C_2H_2

The only free monad radicles known are the two bodies already described, namely, nitrosyl, or nitric oxide, NO, and nitryl, or nitric peroxide, NO_2. Instances of free diad radicles are, however, more numerous. Thus we have

Mercury	Hg''
Zinc	Zn''
Cadmium	Cd''
Carbonic oxide (carbonyl) .	$(CO)''$
Sulphur dioxide (thionyl) . .	$(SO_2)''$
Ethylene	$(C_2H_4)''$
Ammonia	$(NH_3)''$

Molecules of this kind are of the same order as those referred to at the beginning of the chapter; but why in so many cases the number of unemployed units of valency should be an even number has not yet been satisfactorily explained.

Accepting the definition of a 'radicle' given on p. 107, it is obvious that there are a great many commonly recognised radicles which can hardly be expected ever to assume a bodily existence apart from the compounds in which they occur associated with elements of a different chemical character.

In all the carbonates, for example, a group consisting of one atom of carbon and three atoms of oxygen occurs, and this group is capable of being exchanged for Cl_2 or $(OH)_2$ or O by double decomposition. It is, therefore, entitled to be spoken of as a compound radicle, although, by reason

of the large proportion of oxygen it contains, its condition would be that of unstable equilibrium, even if it could assume temporarily an isolated existence.

Similar remarks apply to such radicles as NO_3 (of nitrates), ClO_3 (of chlorates), SO_4 (of sulphates), PO_4 (of phosphates), and the rest, which, under possible experimental conditions, have never yet been isolated.

Further discussion of this question is reserved for the chapter relating to the properties of acids, bases and salts.

The student may be reminded that our system of notation is to be understood and employed only in a unitary sense. Every molecule must be regarded as one entire and undivided unit, whose actions and reactions proceed from the resultant of all the different forces exerted by its several constituent parts. A chemical compound may be compared to a musical chord, constituted, doubtless, of many and complex elements, but communicating to the ear the impression of singleness and harmony. And though there are many cases in which one constituent may have a predominating influence in virtue of its mass or special store of unexhausted energy, it never acts as though it were alone, its behaviour being always modified by the presence of the other elements with which it is associated.

The following memoranda will serve to assist the student in writing the formulæ of many common salts. In order to construct any required formula it is only necessary to place a symbol or group of symbols, taken from under the positive sign, side by side with a symbol or group taken from under the negative sign, and to adjust the quantity of each so as to comply with their respective habits of combination.

Thus let

R' represent a univalent radicle,
R'' „ „ bivalent radicle,
R''' „ „ trivalent radicle, &c.

Then it is only necessary to remember that

R′ combines with R′,
2 R′ „ „ R″,
or R″ „ „ R″,
3 R′ „ „ R‴,
3 R″ „ „ 2 R‴, &c.

In this way the student will readily learn to compose the unitary formulæ of all the most commonly occurring compounds, without risk of falling into any serious error.

VALENCY OF COMMON SALT RADICLES.

Univalent.		Bivalent.		Trivalent		Quadrivalent.		Sexvalent.
−	+	−	+	−	+	−	+	+
F	H	O	Ba	PO_4(ortho)	As	SiO_4 (ortho)	Sn (ic)	
Cl	K	S	Sr	AsO_3	Sb	P_2O_7 (pyro)	Pt	Cr_2 (ic)
Br	Na	SO_3	Ca	AsO_4	Bi			Fe_2 (ic)
I	NH_4	SO_4	Mg	BO_3	Au			Mn_2 (ic)
CN	Ag	S_2O_3	Zn		Al			
HO		CO_3	Cd					
NO_2		C_2O_4	Hg (ic)					
NO_3		$C_4H_4O_6$	Cu (ic)					
ClO		SiO_3 (meta)	Pb					
ClO_2		CrO_4	Fe (ous)					
ClO_3		MnO_4	Mn (ous)					
ClO_4			Sn (ous)					
PO_3 (meta)			Hg_2 (ous)					
$C_2H_3O_2$			Cu_2 (ous)					

CHAPTER VIII.

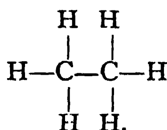
CONSTITUTION.

FROM the explanation given in the preceding chapter it appears that different atoms have different capacities for combination, and that the atoms of many elements have the power of uniting with several others which may be all of the same kind or may be of different kinds. Thus an atom of oxygen may combine with two atoms of hydrogen,

or it may unite into one molecule an atom of hydrogen and an atom of potassium. In order to express clearly the manner in which the valency of each atom in a molecule is supposed to be occupied, a system of formulæ has been devised which will be easily intelligible from the following examples. In the notation here introduced, it must be understood that the symbol placed on the left of a formula represents an atom to which all on the same line are directly united. Thus CH_4 implies that four atoms of hydrogen are combined with one atom of carbon, though they are not directly united with one another. Those also which are connected by a bracket are united together. Thus,

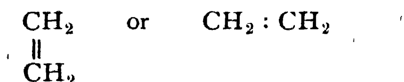


means that there are two atoms of tetrad carbon united by one-fourth of their combining power, while each retains three atoms of hydrogen. The same relations are expressed more clearly in this figure, or 'graphic formula':

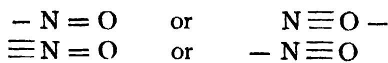


Such compounds are conventionally spoken of as 'saturated' when the valency of each atom present is satisfied. It frequently happens, however, that the valency of one or more atoms in the molecule is not compensated by a sufficient number of associated atoms, and then the compound is spoken of as 'unsaturated.' In such cases the compound usually enters into combination very readily. Thus ammonia NH_3 must be supposed to contain unsaturated nitrogen. Or if from the formula C_2H_6 two atoms of hydrogen be abstracted, the formula of ethylene, C_2H_4, results, and this hydrocarbon combines instantly

with chlorine or bromine. The carbon is unsaturated, and this is usually expressed by placing two lines or points between the symbols of carbon, thus :—



One defect of this formula is that it seems to imply that the two atoms of carbon are united by a stronger tie than that which holds them together in the saturated compound where they are joined by the exercise of one unit of valency of each. As a matter of fact the reverse is the case, the place of the double bond being invariably a point of weakness in the molecule where separation of the united atoms most easily takes place. The custom is to represent the spare valency in the manner shown in the formula, but opinion is divided as to the exact physical meaning to be attached to the expression. Free or unoccupied valencies must be admitted in some cases, as, for example, in nitric oxide, in which whatever valency is attributed to the nitrogen and the oxygen respectively, at least one unit remains unsaturated, thus : —



Of course the lines connecting the symbols are not designed in any case to represent a substantive bond or link, but each represents one unit of valency exercised by the atoms supposed to be united. It often happens that more than one arrangement of symbols would be possible in such a formula. In that case evidence which will help in the choice of a formula may usually be obtained by a careful study of the formation or decomposition of the compound.

Sulphuric acid furnishes a good example of the kind

of fact and argument upon which rational formulæ are based. In this case mere analysis tells us only that the compound contains an atom of sulphur, two atoms of hydrogen, and four atoms of oxygen, or SH_2O_4. But on examination of its salts we find that both the atoms of hydrogen are replaceable by metals; and to indicate this basic function of the hydrogen it is the custom to write it at the beginning of the formula thus :—



$$H_2SO_4.$$

When sulphuric acid is distilled with phosphoric chloride it takes an atom of chlorine from the chloride in exchange for an atom of oxygen and an atom of hydrogen. The resulting compound has the composition expressed by the formula :—



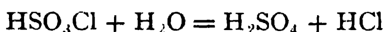
$$HSO_3Cl.$$

If this compound is heated strongly, two molecules of it interact so as to reproduce a molecule of sulphuric acid and a compound having the formula :—



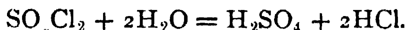
$$SO_2Cl_2.$$

Both of the new compounds reproduce sulphuric acid when dissolved in water, thus :



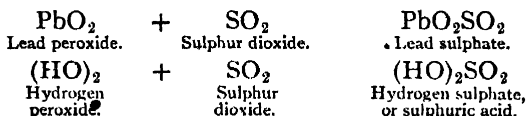
$$HSO_3Cl + H_2O = H_2SO_4 + HCl$$

and



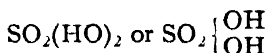
$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

It seems, therefore, that sulphuric acid is capable of breaking up into the groups SO_2 and $2HO$. This is confirmed by the fact of the production of sulphates by the union of sulphur dioxide with peroxides, as in these instances :—



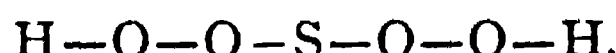
PbO_2 Lead peroxide.	+	SO_2 Sulphur dioxide.	PbO_2SO_2 Lead sulphate.
$(HO)_2$ Hydrogen peroxide.	+	SO_2 Sulphur dioxide.	$(HO)_2SO_2$ Hydrogen sulphate, or sulphuric acid.

Such reactions as these and many others are recalled when we write the formula :—



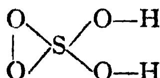
$$SO_2(HO)_2 \text{ or } SO_2\begin{cases}OH\\OH\end{cases}$$

In the present state of knowledge the dissection of the formula cannot be carried with certainty any further, for the manner in which the oxygen is attached to the sulphur is doubtful. The formula may be expanded into the following graphic expressions, but it is not possible to decide which, if any, is the correct expression. If sulphur is assumed to be, like oxygen, bivalent the formula becomes

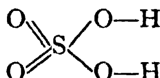


$$H—O—O—S—O—O—H.$$

If sulphur is considered to be quadrivalent the formula may be written

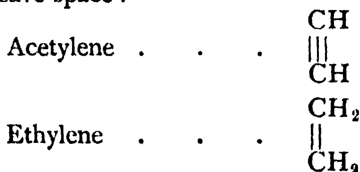


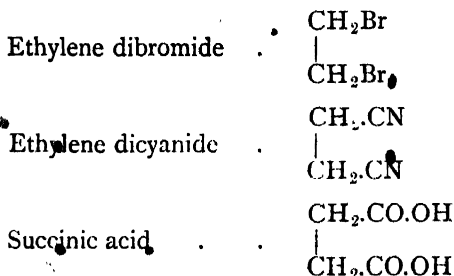
And, lastly, assuming that sulphur is sexvalent the formula is written



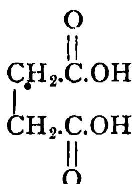
This last expression is most commonly adopted.

The best examples of this kind of investigation are afforded by compounds of carbon. By way of illustration the case of succinic acid, referred to on pp. 92, 93, may be reproduced in the expanded form, a dot being sometimes used instead of a line in accordance with custom and in order to save space :—





or



Formulæ of this kind become indispensable in the study of the phenomena of *isomerism*,[1] a term of very comprehensive significance, but which is usually employed in reference to compounds which, though having the same composition, exhibit different properties. An example will serve to make the matter clear. The nature of the phenomenon will be understood by comparing together several such compounds as the following, all of which are represented by the same molecular formula, $C_3H_6O_2$:—

1. Propionic acid is a crystallisable acid, which, after melting, boils at 140°. It is monobasic, forming one salt only with each of the metals sodium, potassium, and silver. Its rational formula may therefore be written thus: $HC_3H_5O_2$.

2. Ethyl formate is a colourless aromatic liquid, which boils at 56°. When heated with caustic potash it is resolved into ethyl alcohol and potassium formate. This mode of

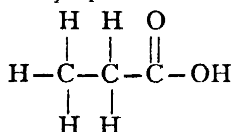
[1] From ἴσος, equal, and μέρος, part.

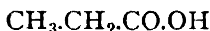
decomposition is recorded when we write the formula thus: $C_2H_5.CHO_2$.

3. Methyl acetate is a colourless, volatile liquid, which also boils at 56°, but when decomposed by an alkali it yields wood spirit (methyl alcohol) and an acetate. So its formula must be $CH_3.C_2H_3O_2$.

If now these formulæ are expanded so as to display fully the valencies of all the constituent atoms, the order will be seen to be very different in each.

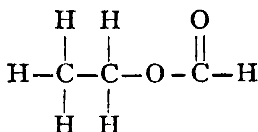
Propionic Acid.

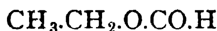


or 

or 

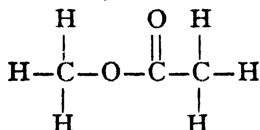
Ethyl Formate.



or 

or 

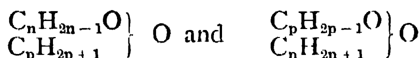
Methyl Acetate.



or 

These three compounds, which have the same composition and molecular weight, but differ in the nature of the products they yield, when decomposed or acted upon by chemical agents, are said to be *metameric* with one another.

Many cases similar to the last two may easily be found among esters (compound ethers), ketones, and other bodies, the molecules of which consist of two compound radicles united together by oxygen or a bivalent group. Pairs of such bodies may be called reciprocal metamerides, because the excess of carbon and hydrogen in one of the radicles is made up for by a corresponding deficiency in the other. General formulæ for such pairs of isomerides among the esters might be written thus :—

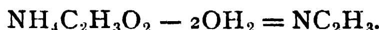


$$\left.\begin{matrix} C_nH_{2n-1}O \\ C_pH_{2p+1} \end{matrix}\right\} O \quad \text{and} \quad \left.\begin{matrix} C_pH_{2p-1}O \\ C_nH_{2n+1} \end{matrix}\right\} O$$

In many cases an extraordinary resemblance in physical properties may be observed in comparing together two compounds of this kind.

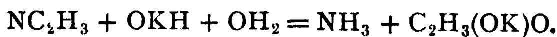
Another instructive example of metameric relations is presented by the two classes of alcoholic cyanides.

1. *Cyanides.*—By distilling ammonium acetate with phosphoric oxide (a substance which has an extraordinary attraction for water) the ammonium salt is converted into a volatile compound, long known as acetonitrile, and boiling at 77°



$$NH_4C_2H_3O_2 - 2OH_2 = NC_2H_3.$$

When acted upon by boiling alkali it yields up its nitrogen in the form of ammonia, and re-generates an acetate



$$NC_2H_3 + OKH + OH_2 = NH_3 + C_2H_3(OK)O.$$

This reaction is explained by supposing that in acetonitrile or methyl cyanide the two atoms of carbon are in

direct union with each other, as represented by this diagram :—



$$N \equiv C - CH_3$$

or $$NC.CH_3.$$

2. *Isocyanides or Carbamines.*—These compounds undergo a different transformation when acted upon by hydrating agents. Notwithstanding that they have the same composition as the cyanides, they are scarcely affected by alkalis, though when boiled with diluted acids they are readily converted into formic acid and bases, in which the nitrogen is associated with part of the carbon. For example, methyl isocyanide treated in this manner yields methylamine and formic acid.



$$\underset{\text{Methyl Isocyanide.}}{NC_2H_3} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Methylamine.}}{N\begin{cases}H\\CH_3\end{cases}} + \underset{\text{Formic Acid.}}{CHO.OH}$$

In these compounds, then, the nitrogen probably forms the link between the two atoms of carbon, in the manner shown by the following graphic formula :—



$$C \equiv N - CH_3$$

or $$CN.CH_3$$

The transformation of ammonium cyanate into urea, the first recorded instance of the production of an 'organic' compound from inorganic materials, is a good example of isomeric change. Ammonium cyanate, NH_4CNO, must be represented constitutionally as follows :—



$$H_4N - N = C = O$$

or $$NH_4 \,.\, N \;:\; CO$$

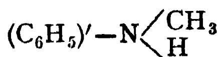
Urea is the amide corresponding to carbonic acid, and is represented by the following formula :—



$$\begin{matrix}H_2N\\H_2N\end{matrix}\!\!>C = O$$

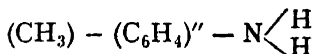
or $$CO(NH_2)_2.$$

Another good illustration of isomeric change is provided by methylaniline :—



$$(C_6H_5)'-N\begin{matrix}\diagup CH_3\\ \diagdown H\end{matrix}$$

which by protracted heating to a high temperature is converted into toluidine, another base in which the methyl group, CH_3, is no longer attached to the nitrogen, but has migrated to a different position within the molecule, and has become attached to carbon, as shown in the following formula :—



$$(CH_3)-(C_6H_4)''-N\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$$

Other examples of isomerism consequent upon internal rearrangement will be explained in a later chapter, but sufficient has now been said to indicate the method of using constitutional formulæ based upon conventional ideas of valency.

From what has gone before it is evident that the properties of bodies are not dependent solely on the nature of the elements of which they are composed. The order of arrangement of the atoms within the molecule determines in all cases the character of the compound, though it must be remembered that some elements, when present in sufficient quantity, are capable of impressing or developing certain features in the compound. Oxygen and other electro-negative elements, for example, tend to generate acid properties in compounds which contain them. The relation of properties to the atomic weights of the elements will be discussed in the section devoted to *Classification*, while the dependence of properties on molecular weight and constitution will be illustrated in the next chapter, and more particularly in the account to be given later of homologous carbon compounds.

CHAPTER IX.

ISOMERISM AND ALLOTROPY.

SUBSTANCES of the same composition but of different properties are said to be *isomeric* with one another. Several examples have already been given in the preceding chapter, but various circumstances connected with the phenomena of isomerism and the several classes of isomerides have now to be considered.

The several cases which present themselves may be discussed under the following heads:

1. Substances having the same composition, the same molecular weight and chemical functions, but different physical properties.

2. Substances having the same composition, the same molecular weight, but different chemical properties and reactions.

3. Substances having the same percentage composition, but different molecular weights.

CLASS I.

When two bodies chemically alike exhibit slight differences of physical characters—such as solubility, crystalline form, relative density, or action upon light, they may be regarded as one and the same substance, though more or less disguised, and such bodies may be distinguished as *physically isomeric*. To this class belong some of the modifications of elemental substances commonly spoken of as their *allotropic* forms or allotropes.

Sulphur, for example, when crystallised from carbon disulphide, yields rhombic octahedrons, the relative density of which is 2·07; whereas, if melted and allowed to cool, it

crystallises in oblique rhombic prisms, having the relative density 1·98. The prismatic variety soon changes spontaneously into the octahedral, which is the stable form, at the same time evolving heat.

Many other examples might be cited of the same substance assuming different crystalline forms, the change of structure being almost invariably attended by differences of density and solubility. One form is generally less stable than the other, and sooner or later, especially under the influence of change of temperature, is converted into the permanent variety.

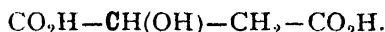
Substances which crystallise in two forms are said to be *dimorphous*. Calc-spar, one form of native calcium carbonate, crystallises in rhombohedrons and other forms belonging to the hexagonal system of crystals, with a density about 2·6. Arragonite, which is also composed of calcium carbonate, forms rhombic prisms of a different system and having a much higher density. Mercuric iodide again is dimorphous, and in this case the two forms differ not only in crystalline form and density but also in colour, the permanent variety being scarlet, while the unstable variety produced by heating the former is bright yellow.

The difference in all these cases probably arises not from any difference in chemical constitution, but from the various modes in which the molecules of the bodies are associated together; such modification being connected with some peculiarity in the circumstances attending their formation.

That a change of molecular structure is accompanied by a corresponding change of physical characters is proved by the well-known fact, that when a piece of glass is strongly compressed or when subject to stress by cooling quickly from a high temperature it acquires the power of polarising light, this property being lost when the strain is relieved.

The most remarkable phenomena, however, are observ-

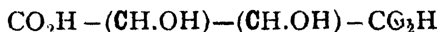
able in such compounds as lactic, malic, and tartaric acids, the sugars and the hydrocarbons called terpenes. These substances in the liquid state, and, when vaporisable as in the case of common turpentine, also in the state of vapour, possess the power of turning the plane of polarisation of a ray of polarised light to the right or to the left. All the substances mentioned above, except common sugar, exist in two forms, which so far as concerns all ordinary chemical characters are indistinguishable from each other, but the one rotates the plane of polarisation to the right, the other to the left. When such substances are crystallisable, like tartaric acid, for example, they exhibit the further peculiarity of producing two varieties of crystals, the faces of which are so situated that the two forms stand towards each other as an object and its image in a mirror. In all such compounds, the constitution of which is known, the molecule contains at least one atom of carbon, having its four units of valency occupied in four different ways. Thus malic acid contains



$$CO_2H-\mathbf{C}H(OH)-CH_2-CO_2H.$$

In this formula we see one of the carbon atoms (printed in heavy type) combined with CO.OH, with H, with OH, and with CH_2. This atom of carbon is said to be *asymmetric.*

Similarly the dextro- and lævo-rotating tartaric acids have the same constitution and no difference between them can be exhibited by the usual formula written on a flat surface

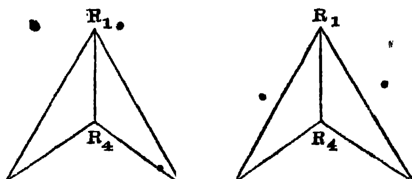


$$CO_2H-(\mathbf{C}H.OH)-(\mathbf{C}H.OH)-CO_2H$$

which contains two asymmetric carbon atoms.

In order to explain the facts it is necessary to appeal to the idea that the relative positions of atoms can be represented in space of three dimensions. The hypothesis originated by Van t'Hoff is now universally adopted, and the name geometrical isomerism or *stereoisomerism* has been

given to the phenomena explained by it. According to this hypothesis the four radicles united to each asymmetric atom are placed at the angles of a regular tetrahedron, the atom of carbon occupying the centre. Two arrangements of the attendant radicles are then possible, the one being a reflection of the other, but not superposible upon it, as shown in the following diagram :—



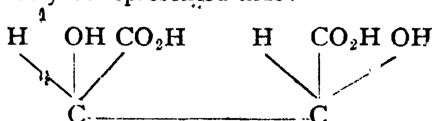
When a compound, the formula of which contains one or more asymmetric carbon atoms, is found to be inactive to the polarised ray, it is usually resolvable into equivalent quantities of two active isomerides, the one rotating to the right, the other to the left. Thus racemic acid is made up of dextro- and lævo-tartaric acids, which may be distinguished thus :—



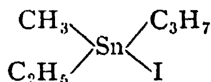
Here each of the atoms of carbon is provided with the same attendant radicles, but in no position is it possible to place the one formula upon the other so that the same radicles come together.

A fourth acid, called mesotartaric acid, which has long been known, is optically inactive, but not resolvable like racemic acid. In dextro- and in lævo-tartaric acids the two asymmetric carbon atoms present carry their attached radicles in the same order, but in mesotartaric acid the dextro-

rotatory effect of one-half of the molecule is neutralised by the lævo-rotatory influence of the other. Hence meso-tartaric acid may be represented thus:—



Quite recently it has been shown that elements other than carbon form compounds of the quadrivalent type which are capable of existing in two forms exhibiting optical activity of the same kind as that shown by carbon compounds. The atoms of such elements—sulphur, tin, lead, and probably others—are therefore capable of forming, like carbon, asymmetric combinations the structure of which is probably also built up on a tetrahedral model. The methyl-ethyl-propyl tin iodide



is an example, but it is at present known only in the dextro-rotatory form.

Nitrogen is also capable of producing asymmetric optically active compounds, and by analogy phosphorus, arsenic, antimony, and other quinquivalent elements, may be expected to yield, when the proper conditions are discovered, combinations having similar properties and constitution.

Class II.

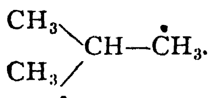
Compounds having the same composition and molecular weight, but different chemical properties, and yielding, when decomposed entirely, different products, have been already referred to in the preceding chapter under the name of metameric compounds. Such things as propionic acid and

ethyl formate are, however, entirely distinct substances, the identity of ultimate composition being merely a matter of accident, and having very little significance. What may be regarded as true *isomerides* in this class are, however, to be found among many orders of carbon compounds. For example, normal butane C_4H_{10} is represented by the formula



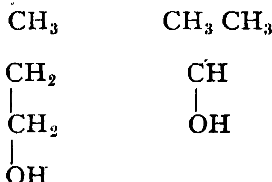
$$CH_3.CH_2.CH_2.CH_3$$

while isobutane, also C_4H_{10}, is



These two compounds are very similar in properties.

Similarly the two propylic alcohols C_3H_8O and C_3H_7HO may be represented by the following formulæ :—



Interesting cases are presented by the 'position' isomerides formed by benzene and other compounds, some of which will be described in Section II.

Class III.—Polymeric Substances.

Bodies containing the same elements united in the same proportion, but having different molecular weights, belong to this class of isomerides. The following are some examples :—

Sulphur boils at 440°, and is converted into an orange-coloured vapour, the density of which, when taken at about 500°, is three times as great as it should be theoretically.

The figures which result from actual experiments are as follows :—

Temperature	Density (H = 1)
468°	114
502°	101
606°	68

At 800° to 1000° it is only 32 times as great as that of hydrogen at the same temperature and pressure, thus conforming with the ordinary rule. There seem, therefore, to be two varieties of the gaseous sulphur molecule, one of which is polymeric with the other. They may be represented by the formulæ



S_2 and S_6.

Ozone, the molecule of which has been shown by various facts and arguments to have the formula O_3, or $\frac{3}{2}O_2$, may also be regarded as polymeric with ordinary oxygen, O_2.

The two varieties of nitric peroxide, NO_2 and N_2O_4, have already been described (p. 107). The latter is polymeric with the former.

Of carbon compounds exhibiting similar relations, the hydrocarbons of the C_nH_{2n}, or olefine series, afford a prominent instance. The formulæ of these bodies are all multiples of the first, methylene, CH_2, which, however, is not known in the free state. Being at once polymeric and homologous with one another, they form similar chemical compounds and exhibit a regular gradation in their boiling points and densities, as shown in the following table.

Name.	Formula.	Boiling Point.
Ethene or ethylene . .	C_2H_4	Gas, liquefiable only under great pressure
Propene or propylene . .	C_3H_6	− 17·8
Tetrene or butylene . .	C_4H_8	3°
Pentene or amylene . .	C_5H_{10}	35
Hexene or hexylene . .	C_6H_{12}	68—70
&c.	&c.	&c.

Further illustrations are supplied by the two chlorides of cyanogen, CNCl and $C_3N_3Cl_3$; by cyanic acid, CNOH, and cyanuric acid, $C_3N_3O_3H_3$; also by the modifications of aldehyd, C_2H_4O, paraldehyd $(C_2H_4O)_3$ or $C_6H_{12}O_3$, metaldehyd, $(C_2H_4O)_n$, and many others.

ALLOTROPY.[1]

Many of the elements are known to exist in the form of two or more modifications, which are very different in physical properties and to some extent also in chemical behaviour. One or two examples have been already referred to under the heads of physical isomerism and polymerism. It is probable that a closer examination of the different cases of allotropy known among the elements would enable us to range them all in one or other of these classes. At present, however, our knowledge will not allow us to adopt with any degree of confidence a final decision upon this point.

In the earlier part of this chapter prismatic sulphur is described as a physical or mechanical modification of the octahedral form of the element, and this is probably correct. But these two are not the only varieties of which this element is susceptible. By heating melted sulphur to a temperature of 240° to 250° it becomes extremely viscid, and if cooled suddenly while in this condition the viscid consistency is retained, and the product is a tough elastic solid quite different in aspect from ordinary sulphur. In this state it is insoluble in carbon bisulphide, a liquid which takes up octahedral sulphur very freely. After keeping a few hours it becomes brittle and crystalline, and recovers its solubility in the usual solvents. The same change may be brought about in a few minutes by plunging it into hot water.

In these transformations, and in the insoluble character of this plastic sulphur, we may trace a close resemblance

[1] From ἄλλος, another, and τροπή, from τρέπω, to turn or change.

to the modifications to which certain carbon compounds, such as aldehyd, cyanic acid, and other bodies, are subject, and which are known to be the effect of polymeric changes. It seems not unreasonable to consider that the production of plastic sulphur may be brought about in the same way.

Phosphorus presents us with an example of a somewhat similar kind. This element in its ordinary state is at common temperatures a solid of waxy consistence, which becomes brittle at low temperatures. Its relative density is 1·82. It melts easily, dissolves in carbon disulphide, and by sublimation or solution it may be obtained in brilliant crystals in the form of regular octahedrons and dodecahedrons. When this body is heated to a temperature approaching 250° it is slowly transformed into a dull red powder or mass, of relative density 2·14, which is no longer soluble in carbon disulphide. It shows itself also in many ways less inclined to enter into chemical combination than common phosphorus, being far less easily imflammable and oxidisable, and unaffected by hot alkaline solutions.

The explanation of this appears, at least very probably, to be that the molecules of the ordinary phosphorus combine together into more complex groupings to form the allotropic molecules, and so expend part of their chemical energy.

Carbon is another element which assumes several distinct forms, the relations of which are of great interest. We may divide these various modifications into two distinct groups, the crystalline and amorphous.

Crystalline carbon is dimorphous. In one form it constitutes the diamond, which crystallises in octahedral forms of the regular system, and has a relative density on the average of 3·3. The other is graphite, or, as it is frequently called, plumbago or black-lead, the crystalline form of which, hexagonal plates, is quite incompatible with the form of the diamond. The average density of graphite is 2·2. If now we review the results which have been obtained by burning the different forms of crystalline carbon, we find

that, allowing for slight experimental errors, the amount of heat evolved by the combustion of equal weights of diamond and graphite are practically the same. Twelve grams of each substance burnt in excess of oxygen disengage enough heat to raise the temperature of about 93,300 grams of water one degree, or, as it is usually expressed, 93,300 units of heat are evolved. The exact numbers in each case are as follows:—

Diamond	93,240	
Natural graphite . . .	93,560	mean
Graphite from iron . .	93,140	93,350.

The smallness of the difference observed would lead one to the belief that graphite and diamond possess the same atomic structure, and that they owe their peculiarities to different arrangement of their molecules—that, in short, they belong to the class of physical isomerides, were it not for some remarkable facts in connection with their behaviour under the influence of chemical reagents. A mixture of nitric acid and potassium chlorate has no action on the diamond, even in a state of the finest dust, but under the influence of this powerful oxidising mixture graphite is converted into a yellow crystalline substance, called by Brodie, who discovered it, graphic acid. This compound contains $C_{11}H_4O_5$ (Brodie), and when heated it decomposes violently, leaving a black graphitic residue, which still retains oxygen and hydrogen.

Amorphous carbon may be obtained by a great variety of processes, and in each case the product exhibits more or less distinctly marked peculiarities.

These varieties of carbon when oxidised yield, beside black soluble substances of indefinite composition, a considerable quantity of an acid called mellitic acid, $C_6(CO_2H)_6$, which is a derivative of benzene. Twelve grams of wood charcoal give out 96,960 units of heat when burnt so as to

form carbonic anhydride, and other kinds of charcoal, when deprived as completely as possible of hydrogen and oxygen, give numbers closely agreeing with this. Taking the average heat of combustion of crystalline carbon as 93,300 units, it is obvious that there is too great a difference here to be fairly accounted for by the hypothesis of experimental error, and consequently that there is some essential difference in the constitution of crystalline and amorphous carbon. The question whether this difference is sufficient to indicate a polymeric relation between these bodies remains to be answered. Silicon and boron form allotropes, which are analogous to those of carbon, and concerning which the same questions may be propounded.

The study of these and many other cases has led to the discovery that the formation of any two isomeric bodies always involves the consumption of different amounts of heat. Also, that when these bodies are burnt, or otherwise similarly decomposed, the disruption of their molecules is attended by the evolution of different amounts of heat.

This is nearly equivalent to saying that in order to produce equal weights of two isomerides different amounts of work must be expended in the two processes, and that different amounts of energy are stored up in the products.

How is this energy disposed of? Adopting the molecular theory, we may reply that the energy is employed in communicating to some atom or atoms within the molecule a new kind of motion or a change of position, whereby it acquires new chemical functions, and this change of function we endeavour to represent by altering the arrangement of the symbols which go to make up the formula of the body.

EXERCISES ON SECTION I.

Corrections of Gas-volumes for Changes of Pressure and Temperature.

1. 100 c.c. of air when bar. = 750 mm. Find the volume when bar. = 790 mm.

2. 250 c.c. of air when bar. = 765 mm. Find the volume when bar. = 745 mm.

3. What pressure in atmospheres would be required to make the density of hydrogen (sp. gr. ·0693) equal to that of air?

4. Calculate the atmospheric pressure per square centimetre when the barometer stands at 760 mm.

Weight of 1 c.c. of mercury, 13·596 grams.

5. Find the atmospheric pressure per square decimetre when the barometer stands at 750 mm.

6. What change of atmospheric pressure will be denoted by a change of 12 mm. in the barometric column?

7. The weight of one litre of hydrogen at 0° and 760 mm. is ·0896 gram or 1 crith. Calculate the weight of one litre of hydrogen measured off under a pressure of 1400 mm.

8. Find the weight of 1 litre of nitrogen (sp. gr. 14); of 10 litres of carbon dioxide (sp. gr. 22); of 250 c.c. of oxygen (sp. gr. 16).

9. A mass of air at 0° measures 100° c.c. What volume will it occupy at 20°; at 15°·5; at 100°?

10. A certain quantity of air is measured at 75°. What volume will it have at 0°?

11. 1000 c.c. of gas at 12°·5. What volume at 75°?

12. 500 c.c. of a gas at 10°. What volume at 40°?

13. 300 c.c. of a gas at 25°. What will its volume be at − 10°?

14. 75 c.c. of nitrogen measured at 50°. What volume at − 35°?

15. 1500 c.c. of hydrogen measured at 20°. At what temperature will it measure 1000 c.c.?

16. Five degrees centigrade correspond with nine degrees on the Fahrenheit scale. Find the coefficient of expansion of gases for 1° F.

17. 150 c.c. of nitrogen are measured at 10°, and under a pressure of 500 mm. of mercury. What will the volume become at 16°·4 when the pressure is 540 mm.?

18. A quantity of nitrogen confined in a tube standing over mercury in a mercurial trough measures 75·5 c.c.; temp. 15°; bar. 742 mm.; surface of mercury inside the tube above surface of mercury in the trough 122 mm. Find the volume which the gas would occupy at normal temperature and pressure.

19. 1000 cubic feet of gas are put into a balloon of 1250 cubic feet capacity; temp. 18°; bar. 765 mm. After ascending a certain height it is found to be fully distended. What is the atmospheric pressure, temperature being 8°?

20. A certain balloon is just capable of holding 10 grams of hydrogen under standard conditions: what is its capacity? How much larger must it be made if it is required to sustain a diminished atmospheric pressure equal to 650 mm. bar?

Diffusion of Gases.

21. The specific gravity of chlorine is 35·5 (H = 1). Compare its velocity of diffusion with that of hydrogen.

22. Specific gravity of ozone, 24; of carbon dioxide, 22. Compare their velocities of diffusion with each other and with that of H (sp. gr. 1).

23. The rate of diffusion of a gas is observed to be ·81 when that of air is 1. Find its density.

24. Oxygen and hydrogen are separated by a porous plate, and 3·83 cubic centimetres of hydrogen pass through the plate in a second. What volume of oxygen passes during the same time in the opposite direction?

25. In the last question suppose the original volume of the oxygen to have been 20 c.c.; what will be the composition of the mixture formed in its place after three seconds, assuming the apparatus so arranged that no change of pressure occurs?

Laws of Combination. Symbols and Formulæ.

26. Two elements, A and B, unite together in the following proportions by weight: show that they satisfy the law of multiple proportions:—

	A	B
I.	96·28	3·72
II.	92·83	7·17
III.	89·62	10·30
IV.	86·62	13·38

27. 100 volumes of each of the following gases contain respectively the amounts of nitrogen and oxygen given: illustrate the law of multiple proportions by means of these numbers:—

	Nitrogen	Oxygen
Nitrous oxide	100	50
Nitric oxide	50	50
Nitric peroxide	100	200

28. Give the names of the elements represented by the following symbols: Al, Sb, Fe, Mg, Hg, Mn, Ca, C, Cl, I, N, P, K, S, Ag, Na, Br, Cu, F, H, Pb, O, Si, Zn.

29. Write down the symbols and atomic weights of

Barium, boron, bromine;
Calcium, carbon, copper;
Magnesium, manganese, mercury, silver;
Phosphorus, potassium, lead;
Sulphur, sodium, silicon;
Iron, iodine, chlorine, oxygen, nitrogen.

30. Read these symbols and formulæ thus:—

N_2 represents one molecule of nitrogen, consisting of two atoms;
O, O_2, OH_2, $2OH_2$, HCl, H_2, Cl_2, NH_3, H_3PO_4, H_2SO_4, $FeSO_4$, $2FeSO_4$, $Al_2(SO_4)_3$, $12OH_2$, $12Al_2(SO_4)_3$, CO_2, $3CO_2$.

31. Write down the formulæ and molecular weights of water, ammonia, hydrogen chloride, carbon dioxide, sulphuric acid, ferrous sulphate, aluminic sulphate, phosphoric acid.

32. Write down the whole weight represented by each of the following expressions: $2HgO$, $10OH_2$, $3FeS$, $3FeS_2$, $2CS_2$, $KC_4H_5O_6$, $K_2C_4H_4O_6$, $5C_7H_9N$, $12CH_4$, $KAl(SO_4)_2 + 12OH_2$, $3[NH_4Cr(SO_4)_2 + 12OH_2]$.

33. Name the following compounds: BaO, CaO, MgO, ZnS, KCl, $NaBr$, AgF, H_2S, HI, KCN, SSe, BN, H_3P.

34. BaO, BaO_2; Hg_2O, HgO; FeS, FeS_2; MnO, Mn_2O_3, MnO_2; FeO, Fe_2O_3, Fe_3O_4; N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5; P_2S_3, P_2S_5; $SnCl_2$, $SnCl_4$; $FeBr_2$, Fe_2Br_6; Cu_2Cl_2, $CuCl_2$; $CrCl_2$, Cr_2Cl_6, CrF_6; $SbBr_3$, $SbBr_5$.

35. KNO_2, KNO_3 (—ate); K_2SO_3, K_2SO_4 (—ate); KCl, $KClO$, $KClO_2$, $KClO_3$ (—ate), $KClO_4$; KI, KIO_3 (—ate), KIO_4; $NaHSO_3$, Na_2SO_3; Na_2HPO_4, Na_3PO_4, NaH_2PO_4; H_3PO_2, H_3PO_3, H_3PO_4 (—ic); HCl, $HClO$, $HBrO$, $HClO_2$, $HClO_3$, HIO_3, $HClO_4$, $HBrO_4$.

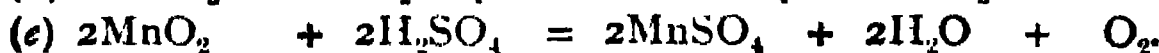
36. Write out the following equations according to the scheme on p. 54:—

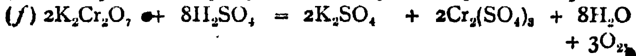

(*a*) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$.


(*b*) $2KI + Cl_2 = 2KCl + I_2$.


(*c*) $SO_2 + 2OH_2 + Cl_2 = H_2SO_4 + 2HCl$.


(*d*) $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$.


(*e*) $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$.


(*f*) $2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$.

37. Write out the following equations according to the scheme on p. 55 :—

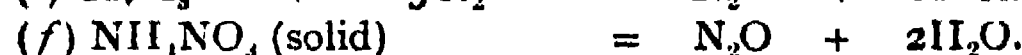

(a) $2OH_2 + 2Cl_2 = 4HCl + O_2$.


(b) $CO_2 + C$ (solid) $= 2CO$.


(c) $2CO + O_2 = 2CO_2$.


(d) $2NH_3 = N_2 + 3H_2$


(e) $2NH_3 + 3Cl_2 = N_2 + 6HCl$.


(f) NH_4NO_3 (solid) $= N_2O + 2H_2O$.

38. Write out in symbolic equations :—

(a) Ammonium chloride and calcium hydroxide give ammonia, calcium chloride, and water.

(b) Ammonium nitrite (heated) yields nitrogen and water.

(c) Common salt and sulphuric acid yield sodium hydrogen sulphate, and hydrogen chloride.

(d) Copper and nitric acid yield copper nitrate, nitric oxide, and water.

(e) Mercury and sulphuric acid yield mercuric sulphate, sulphur dioxide, and water.

(f) Antimonious sulphide and hydrochloric acid yield antimonious chloride and sulphuretted hydrogen.

39. How many grams of oxygen are required to burn 24 grams of carbon and 32 grams of sulphur?

40. How many pounds of zinc are there in 350 pounds of the sulphate $ZnSO_4$?

41. How much sulphur will give 100 kilograms of sulphuric acid, H_2SO_4?

42. How many pounds of black oxide of manganese are required to yield, by the action of hydrochloric acid, 112 pounds of chlorine?

43. How many pounds of chalk containing 96 per cent. of calcium carbonate, $CaCO_3$, will neutralise 250 pounds of sulphuric acid?

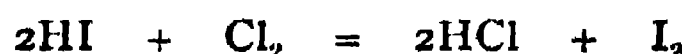
(In the following examples the gases are supposed to be at normal temperature and pressure.)

44. Find the weight of 20 litres of oxygen, of 50 litres of chlorine, of 250 litres of ammonia.

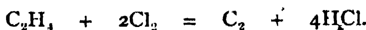
45. How many litres of oxygen are required to combine with

α. 12 criths of carbon? β. 2 grams of sulphur?
γ. 10 grams of carbon?

46. How many litres of chlorine are required to decompose 12 litres of hydrogen iodide?


$$2HI + Cl_2 = 2HCl + I_2$$

47. How many litres of chlorine are required for the complete decomposition of 10 litres of olefiant gas?



$$C_2H_4 \quad + \quad 2Cl_2 \quad = \quad C_2 \quad + \quad 4HCl.$$

48. How many litres of hydrogen are obtained by dissolving 10 grams of magnesium in an acid?

49. What weight of potassium chlorate is required to yield 35,000 cubic centimetres of oxygen?

50. What materials and what quantities would you employ in order to obtain 50 litres of each of the oxides of carbon?

51. How much mercuric cyanide, $Hg(CN)_2$, must be used to furnish 50 c.c. of cyanogen, C_2N_2, assuming that 60 per cent. of the cyanogen is obtained in the gaseous form?

52. Red oxide of copper contains 88·8 parts of copper and 11·2 parts of oxygen by weight; black oxide of copper contains 79·87 of copper and 20·13 of oxygen. If the formula of the black oxide is CuO, how should the red oxide be represented?

53. Water contains 88·8 of oxygen, 11·1 of hydrogen. If its formula is OH_2, find the formula for peroxide of hydrogen, which contains 94·12 O and 5·88 H.

54. Two hydrocarbons have the following composition:—

	I.		II.
Carbon . .	85·71	$\}= C_2H_4$	92·3
Hydrogen . .	14·29		7·7

Find the formula for II.

55. Show that the composition of the oxides of nitrogen, of manganese, and of chromium are in accordance with the law of multiple proportion.

56. Examine the following equations, attach the name to each formula, and classify the reactions according to Chapter III., p. 57, giving reasons in doubtful cases:—

(*a*) $Na_2 + 2OH_2 = 2ONaH + H_2$

(*b*) $Fe + H_2SO_4.H_2O = FeSO_4.H_2O + H_2$

(*c*) (electrolysis) $2HCl = H_2 + Cl_2$

(*d*) $SO_2 + H_2O_2 = H_2SO_4$

(*e*) (heat) $+ 3MnO_2 = Mn_3O_4 + O_2$

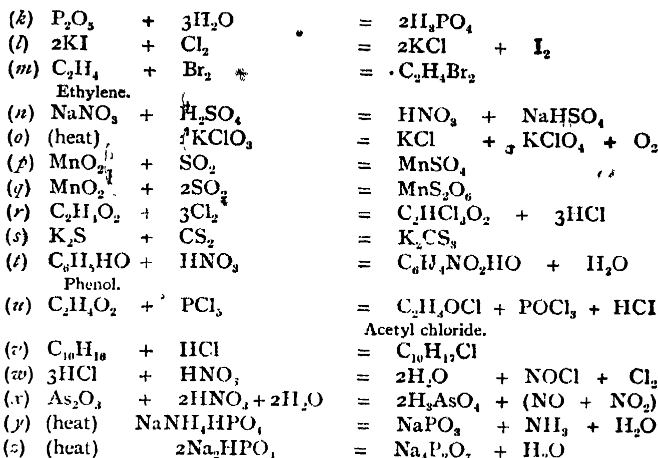
(*f*) $OKH + HCl = KCl + OH_2$

(*g*) $O_2H_2 + O_3$ (ozone) $= OH_2 + 2O_2$

(*h*) $SO_3 + H_2O = H_2SO_4$

(*i*) $PH_3 + HI = PH_4I$

(*j*) $N_2O_5 + H_2O = 2HNO_3$



(*k*) $P_2O_5 + 3H_2O = 2H_3PO_4$

(*l*) $2KI + Cl_2 = 2KCl + I_2$

(*m*) $C_2H_4 + Br_2 = C_2H_4Br_2$
Ethylene.

(*n*) $NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$

(*o*) (heat) $KClO_3 = KCl + KClO_4 + O_2$

(*p*) $MnO_2 + SO_2 = MnSO_4$

(*q*) $MnO_2 + 2SO_2 = MnS_2O_6$

(*r*) $C_2H_4O_2 + 3Cl_2 = C_2HCl_3O_2 + 3HCl$

(*s*) $K_2S + CS_2 = K_2CS_3$

(*t*) $C_6H_5HO + HNO_3 = C_6H_4NO_2HO + H_2O$
Phenol.

(*u*) $C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl$
Acetyl chloride.

(*v*) $C_{10}H_{16} + HCl = C_{10}H_{17}Cl$

(*w*) $3HCl + HNO_3 = 2H_2O + NOCl + Cl_2$

(*x*) $As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + (NO + NO_2)$

(*y*) (heat) $NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$

(*z*) (heat) $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$

57. How many cubic centimetres of ammonia (measured at 15° and under 740 mm.) would be obtained from $53\frac{1}{2}$ grams of ammonium chloride?

58. How many cubic centimetres of sulphur dioxide (measured at 20° and 740 mm.) can be obtained by the action of copper on 20 grams of sulphuric acid?

Atomic and Molecular Weights.

59. One atom of antimony is said to be equivalent to three, and one atom of zinc to two, atoms of sodium. Explain this statement.

60. Distinguish between atomic, equivalent, and molecular weights.

Give the atomic and equivalent weights of mercury, zinc, chlorine, iodine, sulphur, iron, and copper.

Also write down the molecular weights of H_2S, PCl_5, AsH_3, H_2SO_4.

61. What weight of sulphuric acid can be precipitated by one gram of barium chloride?

62. What is the weight and volume (at normal temperature and pressure) of the hydrogen contained in 10 grams of microcosmic salt, $NaNH_4HPO_4.4H_2O$?

63. Enumerate very briefly the various methods by which atomic weights may be determined; and indicate in the case of each of the following elements the method or methods which would be applicable:

oxygen, chlorine, potassium, mercury, carbon, sulphur, lead, silver, arsenic, silicon, barium, copper, manganese.

64. The specific heat of iron is ·1138. State approximately its atomic weight.

65. The specific heat of cadmium is ·0567, and its equivalent 56. Give its atomic weight.

66. The equivalent of platinum is 48·75, and its perchloride has the formula $PtCl_4$. Find its specific heat.

67. The formula of water was formerly written thus, HO, and subsequently, for some years, H_2O_2 (assuming O = 8). Discuss both these formulæ, pointing out any inconsistencies you may detect in them.

68. Complete the equation



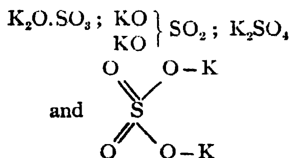
$$Ag_2O \qquad H_2O_2 =$$

Quote analogous reactions, and explain the theoretical significance of these facts.

69. The volume of the molecule of a compound body in the gaseous state is double the volume of the atom of hydrogen. Examine the truth of this statement; give the experimental facts upon which it is based, and discuss any exceptions to it with which you are acquainted.

70. Acetic acid contains C 40, H 6·6, and O 53·4 per cent.; and chloracetic acid contains 37·5 per cent. of chlorine. Calculate the molecular weight of acetic acid.

71. Explain the signification of the several formulæ for potassic sulphate,



$$K_2O.SO_3\ ;\ \left.\begin{matrix}KO\\KO\end{matrix}\right\}SO_2\ ;\ K_2SO_4$$

and

72. With the help of the table on p. 112 write down the formulæ of the following salts: sodium fluoride, silver sulphate, mercuric cyanide, mercurous phosphate, barium chlorate, bismuth chloride, ferrous orthosilicate, cupric acetate, ferric nitrate, chromic oxalate, stannic phosphate, calcium hypochlorite, &c. &c.

73. Write the formulæ of nitric oxide, carbonic oxide, white arsenic, acetic acid, benzoic acid, oxalic acid, aluminium chloride, ferric chloride, orthophosphoric acid, and describe briefly the method or methods by which the molecular weight of each has been determined.

74. If the specific heat of a metal is ·03, state approximately its atomic weight. Calculate the exact value of the atomic weight, the

composition of the chloride being, metal 2·915 parts to 1 part of chlorine by weight.

75. The atomic weight of silver being 108, and its specific heat ·057, another metal M, of which 70 parts unite with 35·5 parts of chlorine, is found to have the specific heat ·0306. What is the atomic weight of this metal and the formula of its chloride?

76. From the following observations determine the molecular weights of the dissolved substances:—

Freezing point of water used, 0·000°. Weight of substance, 12·616 grams. Weight of water, 92·25 grams. Freezing point of solution, −1·450°.

77. Weight of substance, 13·052 grams Weight of water, 91·98 grams. Freezing point of solution, −0·825°.

78. Freezing point of water used, +0·025°. Weight of substance, 4·9818 grams. Weight of water, 96·94 grams. Freezing point of solution, −0·270°.

79. Freezing point of acetic acid, 3·120°. Weight of substance, 0·8579 gram. Weight of acetic acid, 103·62 grams. Freezing point of solution, 2·970°.

80. Freezing point of benzene, 1·560°. Weight of substance, 0·7815 grams. Weight of benzene, 85·61 grams. Freezing point of solution, 1·350°.

Substance dissolved in 100 grams of ether and observed rise of boiling point:—

81. Benzoic acid, weight of substance, 1·846; rise of boiling point, 0·325°.

82. Camphor, weight of substance, 1·76; rise of boiling point, 0·240°.

83. Phenol, weight of substance, 4·641; rise of boiling point, 1·010°.

84. Weight of alcohol taken, 54·70 grams. Weight of substance dissolved, 0·7222 grams. Boiling point of alcohol, 78·3°. Boiling point of solution, 78·545°.

85. Weight of alcohol taken, 49·82 grams. Weight of substance dissolved, 1·5157 grams. Elevation of boiling point, 0·288°.

86. Weight of water taken, 41·73 grams. Weight of sugar dissolved, 2·0271 grams. Elevation of boiling point, 0·069°. Molecular elevation for 100 grams water = 5·2.

87. Alcohol, ether, and acetic ether have the following rational formulæ:



$$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O, \quad \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O, \quad \left.\begin{matrix} C_2H_5 \\ C_2H_3O \end{matrix}\right\} O$$

What arguments could you draw from the existence of such bodies in favour of the number 16 as the atomic weight of oxygen? Why is it probably neither 8 nor 32?

88. The formula of the molecule or chemical unit of ammonia is NH_3. What is the meaning of this formula, and what are the reasons for using it?

Formula Calculated from Results of Analysis.

89. A compound is found by analysis to have the following composition:—

Carbon	52·18
Hydrogen	13·04
Oxygen	34·78
	100·00

To find its simplest formula.

90. The analysis of a compound leads to these numbers:—

Carbon	37·20
Hydrogen	7·90
Chlorine	54·95
	100·05

It is not often that the formula can be calculated so easily as in the example given in the text and in the last exercise. It must be borne in mind that in actual practice a slight loss is incurred in the estimation of many elements. The number for hydrogen, however, often comes out a trifle too high. Oxygen is always estimated by taking the difference between the total weight of the body analysed and the sum of the weights of the constituents which have been actually weighed.

In the present example we proceed in the following manner:—

Divide the percentages by the atomic weights in the usual way:

$$\frac{37·2}{12} = 3·1 \text{ atoms of carbon.}$$

$$\frac{7·9}{1} = 7·9 \text{ ,, ,, hydrogen.}$$

$$\frac{54·95}{35·5} = 1·54 \text{ atom of chlorine.}$$

Divide the three quotients by the last, which is the least.

$$\frac{3·1}{1·54} = 2·01 \text{ atoms of carbon.}$$

$$\frac{7·9}{1·54} = 5·12 \text{ ,, ,, hydrogen.}$$

$$\frac{1·54}{1·54} = 1 \text{ atom of chlorine.}$$

Now, recollecting that the percentages found by analysis are not exactly true, but only close approximations to the correct numbers, and remembering that the hydrogen is generally in slight excess, we may safely reject the two small fractions which occur in the above numbers, and the formula then reads



$$C_2H_5Cl.$$

To prove that this represents correctly the composition of the body, it is well to recalculate the percentages on the basis of this formula. This calculation is performed in the following manner :—

$$C_2 = 12 \times 2 = 24$$
$$H_5 = 1 \times 5 = 5$$
$$Cl = 35{\cdot}5$$
$$64{\cdot}5$$

$$\text{Then } \frac{24 \times 100}{64{\cdot}5} = 37{\cdot}20$$

$$\frac{5 \times 100}{64{\cdot}5} = 7{\cdot}75$$

$$\frac{35{\cdot}5 \times 100}{64{\cdot}5} = 55{\cdot}03$$

And these theoretical numbers are seen to be very close to those obtained by experiment.

	Theory.	Experiment.
C	37·20	37·20
H	7·75	7·90
Cl	55·05	54·95

91. What is the simplest formula you would assign to a substance containing—

Carbon	54·5
Hydrogen	9·2
Oxygen	36·3

in 100 parts ?

92. Also to the following body :—

Carbon	88·20
Hydrogen	11·80
	100·00

93. And again to an organic base containing —

Carbon	63·78
Hydrogen	5·76
Nitrogen	3·32
Oxygen	27·14
	100·00

94. From the following percentages calculate formulæ for the several compounds:—

I.

Iron	60·5
Sulphur	39·5

II.

Iron	70
Oxygen	30

III.

Hydrogen	5·88
Oxygen	94·12

IV.

Sodium	32·79
Aluminium	13·02
Fluorine	54·19

V.

Carbon	39·31
Hydrogen	7·71
Oxygen	52·98

VI.

Carbon	68·67
Hydrogen	4·95
Oxygen	26·38

VII.

Carbon	49·05
Hydrogen	5·14
Nitrogen	28·61
Oxygen	17·20

VIII

Carbon	42·00
Hydrogen	6·46
Oxygen	51·54

IX.

Carbon	35·71
Hydrogen	2·38
Nitrogen	33·33
Oxygen	28·58

95. Find the formula of nitrosopinene from these numbers:

Carbon	72·57	in 100 parts.
Hydrogen	8·97	
Nitrogen	8·74	

and for nitrosopinene hydrochloride from the following percentages:

Carbon	59·58
Hydrogen	8·07
Nitrogen	7·20
Chlorine	17·45

96. The silver salt of an organic acid was found by analysis to yield 47·1 per cent. of metallic silver. Determine its molecular weight.

In the formation of the silver salt from the acid, 108 parts of silver take the place of 1 part of hydrogen. Therefore,

$$\text{Molec. wt. of acid} - 1 = \text{molec. wt. of salt} - 108$$

or $$\text{Molec. wt. of acid} = \text{molec. wt. of salt} - 108 + 1.$$

In the example given 47·1 parts of silver are contained in 100 parts of the salt. So that 108 parts of silver are contained in $\frac{108 \times 100}{47\cdot1} = 229\cdot3$ parts of the salt. This is, therefore, a number identical with, or very near to, its molecular weight. The answer is, therefore,

$$\text{Molec. wt. required} = 229\cdot3 - 108 + 1 = 122\cdot3.$$

Or, since the atomic weights of carbon, hydrogen, oxygen, and nitrogen are all integers, the fraction must be discarded, and the number becomes 122.

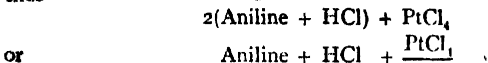
This corresponds with the formula of benzoic acid; verify it

97. Aniline contains—

Carbon	77·4	per cent.
Hydrogen	7·5	
Nitrogen	15·0	

and its platino-chloride contains 32·9 per cent. of platinum: to find its molecular weight and formula.

As explained in Chapter VI. p. 95, the platinum salts of nitrogenous bases are constituted on the same type as that of ammonia. Hence we may represent the formula of platino-chloride of aniline thus—



$$2(\text{Aniline} + \text{HCl}) + \text{PtCl}_4$$

or $$\text{Aniline} + \text{HCl} + \frac{\text{PtCl}_4}{}$$

The first question, then, is, what weight of platinum salt is represented by this formula? This is answered as follows:—

32·9 parts of platinum makes 100 parts of platinum salt;

therefore 195 parts or one atom of platinum make $\frac{100 \times 195}{32 \cdot 9}$ parts, or 592.

We have now to subtract from this the platinum perchloride and hydrogen chloride; half the remainder is the molecular weight of the aniline.

$$592 - 337 - 73 = 182$$

and $$\frac{182}{2} = 91.$$

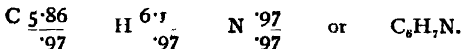
Now, taking the percentage composition of aniline, we have to calculate the proportions of the three elements contained in 91 parts of the base,

$$100 : 91 : : 77 \cdot 4 : x$$
$$x = 70 \cdot 4 \text{ carbon.}$$
$$100 : 91 : : 7 \cdot 5 : y$$
$$y = 6 \cdot 8 \text{ hydrogen.}$$
$$100 : 91 : : 15 \cdot 0 : z$$
$$z = 13 \cdot 6 \text{ nitrogen.}$$

Hence the formula is obtained by dividing these numbers by the respective atomic weights.

$$\frac{70 \cdot 4}{12} = 5 \cdot 86 \text{ atoms of carbon.}$$
$$\frac{6 \cdot 8}{1} = 6 \cdot 8 \text{ atoms of hydrogen.}$$
$$\frac{13 \cdot 6}{14} = \cdot 97 \text{ atom of nitrogen.}$$

Hence, allowing for experimental error, which in this case is very small, the molecular formula required is



$$C\frac{5 \cdot 86}{\cdot 97} \quad H\frac{6 \cdot 1}{\cdot 97} \quad N\frac{\cdot 97}{\cdot 97} \quad \text{or} \quad C_6H_7N.$$

98. ·1442 gram of anthraflavic acid gave ·3712 gram of CO_2 and ·0448 gram of water. Calculate a formula.

99. A sulphide of tellurium and arsenic was analysed. ·6347 gram of the mineral gave ·2584 gram of tellurium, ·3978 gram of ammonio-magnesium arsenate ($MgNH_4AsO_4.H_2O$), and 1·6453 gram of barium sulphate. Calculate a formula.

100. The analysis of trichloracetyl urea gave the following results :—

(*a*) ·3210 gram gave ·2060 gram of CO_2 and ·0453 gram of H_2O ;
(*b*) ·0825 gram gave ·0109 gram of nitrogen ;
(*c*) ·1204 gram gave ·2510 gram of AgCl.

Calculate the formula of the compound.

101. Analysis of uranium pentachloride :—

Weight of substance taken	. . . .	·8955 gram
,, ,, U_3O_8 found	. . . .	·6038 ,,
,, ,, AgCl ,,	. . . .	1·4997 ,,

Calculate the formula.

102. ·3807 gram of benzoic acid gave ·9575 gram of CO_2 and ·1698 gram of water. And ·4287 gram of benzoate of silver gave ·2020 of silver. Calculate the rational formula of benzoic acid.

103. ·5828 gram of platino-chloride of caffeine left after ignition ·143 gram of platinum. What are the molecular weight and formula of caffeine, which contains

Carbon	49·05	per cent. ?
Hydrogen	5·14	
Nitrogen	28·61	
Oxygen	17·20	

104. The platinum salt of a volatile organic base was found by analysis to have the following percentage composition :—Carbon, 9·5 ; hydrogen, 3·2 ; nitrogen, 5·7 ; chlorine, 42·0 ; and platinum, 39·0. The vapour density of the base was found to be 1·59 (air = 1). Calculate from these data its molecular formula.

105. The silver salt of an organic acid contained 62·44 per cent. of metallic silver. It also contains 17·34 per cent. of carbon and 1·73 per cent. of hydrogen. From these data endeavour to find a formula for the acid.

106. Write graphic constitutional formulæ for all possible isomeric forms of the hydrocarbon hexane C_6H_{14}.

107. Write graphic constitutional formulæ for the possible isomeric forms of amyl alcohol $C_5H_{11}(OH)'$, the oxygen being in all cases in the form of hydroxyl as indicated.

108. Write graphic formulæ for methyl acetate and ethyl formate, and for methyl cyanide and acetonitrile.

SECTION II.

CLASSIFICATION.



CHAPTER X.

CLASSIFICATION OF ELEMENTS.

A CLASS is an order or number of things which have common characters or which answer to the same description, and classification is the process of arranging things in classes. The extent of each class and the number of things included in it will depend upon the features or properties which are to be considered as belonging exclusively to the class, and distinguishing it from all other classes. In chemistry we have to consider the composition of matter and all its properties, but especially those which seem to be connected with chemical action. The first division of materials as seen from the chemical point of view is into the two great classes, *Elements* and *Compounds*. A sufficient definition of an element in the modern chemical sense has already been given (p. 30), and the methods and characters by which pure chemical compounds can be distinguished from mechanical mixtures have been given at some length (pp. 36 to 41).

We may now proceed to consider the rules by which a

classification of both elements and compounds may be most usefully effected.

Elements might be divided into solids, liquids, and gases, but such an arrangement, being based only upon accidental physical conditions, would obviously be useless for all scientific purposes. To secure a classification which not only serves the purpose of assisting the memory but also brings to view analogies or relationships which would otherwise remain unnoticed, it is necessary to adopt such a system that the members of each class agree not only in one character, as in being solid or lustrous or heavy, but in as many characters as possible. The student must, however, be warned that whatever system is adopted it is impossible, in attempting the classification of the things of nature, so to define a class as to separate every individual in the class from every other individual which is not included in it. The natural families or groups into which the elements are divisible provide many examples of substances which in some minor particulars present exceptional characters.

The earliest recognised class among the elements is that which has so long been known as the Metals. The division of the known elements into metals and non-metals is, however, in some respects unsatisfactory, and has become insufficient since the discovery of the elements of the Argon group. We may now arrange the known elements in two divisions as follows :—

Division I.—Inactive Elements.

All exist in the free state, and are not known to form any chemical combination either among themselves or with any of the remaining elements.

All at present known are colourless gases having different densities, and, it is believed, monatomic molecules.

Their names, approximate densities, and molecular weights are as follows :—

Name.	Density.	Molecular Weight.
Helium . . .	2	4
Neon . . .	10	20
Argon . . .	20	40
Krypton . . .	41	82
Xenon . . .	64	128

DIVISION II.—ACTIVE ELEMENTS.

This division includes all the ordinary components of the earth's crust and atmosphere. They are distinguished from the elements in Division I. by entering into a great variety of combinations. They admit of being arranged in three classes as follows :—

Class I.—*Non-metallic*, or Electro-negative Elements.

Class II.—*Metalloids*, or Imperfect Metals, generally electropositive.

Class III.—*Metals.* Electropositive.

CLASS I.—NON-METALLIC ELEMENTS.

Gaseous at common temperatures :

Oxygen, nitrogen, fluorine, chlorine.

Liquid at common temperatures :

Bromine. Density, 2·96.

Solids

Sulphur (octahedral),	*Density*,	2·07
Phosphorus (red)	,,	2·2
Silicon (graphitic)	,,	2·49
Boron (crystalline)	,,	2·6
Carbon (diamond)	,,	3·5
Selenion (crystalline)	,,	4·5
Iodine	,,	4·95

These elements, as a class, are characterised by no community of physical properties. At common temperatures and pressures four are gases—fluorine, chlorine, oxygen, nitrogen ; one, bromine, is a liquid ; the rest are brittle solids, the density of which is in no case very high. Of these, iodine, sulphur, selenion, and phosphorus are fusible and vaporisable ; the remaining three are distinguished by difficult fusibility and volatility, by abnormal specific heats (p. 74), and by affording, in the cases of graphitic carbon and silicon, the only notable examples among the non-metals of electric conductivity.

In their chemical characteristics, however, there is tolerable uniformity. They all combine with hydrogen, forming gaseous or very volatile hydrides ; they also combine with metals, often in several proportions ; their oxides are either neutral and indifferent bodies, like carbonic oxide, or, the great majority, anhydrides, which by uniting with water form acids. In the electrolysis of their compounds the non-metals are invariably liberated at the anode, and they are usually spoken of as negative elements. There are several among them, however (carbon, silicon, and boron certainly, and probably nitrogen), which have not been observed as primary products of electro-chemical decomposition, and in such cases it is only possible to infer from analogy that, like the rest of the non-metals, they are probably capable of forming negative ions.

NON-METALS.—GROUP I : THE HALOGENS.

	Symbols.		*Atomic Weights.*
Fluorine .	F	=	19
Chlorine .	Cl	=	35·45
Bromine .	Br	=	79·96
Iodine . .	I	=	126·85

$$\frac{Cl + I}{2} = 81·15$$

These elements are characterised by a remarkable family likeness. The last three especially are constantly associated

together in nature in the haloid[1] salts of potassium, sodium, &c., and in the ores of mercury, silver, and other heavy metals. They also agree very closely with one another in their general physical characters and chemical deportment.

At ordinary temperatures chlorine is gaseous, bromine liquid, iodine solid; but bromine and iodine are volatile, and yield heavy, coloured vapours, which, when largely diluted with air, have nearly the same odour as chlorine. Each forms with hydrogen a strongly acid compound, which under ordinary conditions is a colourless, fuming, very soluble gas, consisting of equal volumes of hydrogen and the vapour of the halogen, united without contraction. The chlorides, bromides, and iodides of the alkali metals crystallise in the same form, and the isomorphus replacement of the one halogen by another is observed in a great many other cases.

The following table exhibits the formulæ of all the known oxides and acids of chlorine, bromine, and iodine, from which it will be seen that although there are many gaps to be filled up, perhaps by future research, the correspondence, so far as it goes, is almost complete :—

Halogen Oxides and Corresponding Acids.

	Cl_2O		ClO_2		
HCl	HClO	$HClO_2$	$HClO_2$ } $HClO_3$	$HClO_3$	$HClO_4$
		No oxide of bromine known.			
HBr	HBrO			$HBrO_3$	
				I_2O_5	
HI	HIO (?)			HIO_3 (?) or $H_2I_2O_6$	HIO_4 (?) or H_5IO_6

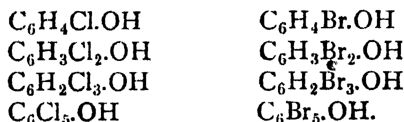
The differences exhibited by chlorine, bromine, and iodine are strictly gradational; chlorine, with the smallest atomic weight, is most active, bromine stands next, and

[1] ἅλς = sea-salt = common salt.

iodine is the least energetic of the three. These differences are manifested by their relative activity towards the metals and hydrogen, chlorine displacing bromine, and bromine displacing iodine from such combinations.

Indications of the same differences are afforded by the superior activity of chlorine as a bleaching agent, and by the energy with which it replaces hydrogen in carbon compounds. In this case chemical activity diminishes in proportion to increase of atomic weight, and rise of boiling-point and density.

The replacement of one or more atoms of hydrogen in a hydrocarbon by an equivalent quantity of one of the halogens produces a neutral substitution compound; but if a similar replacement is effected in the molecule of a body which contains oxygen, the product not unfrequently presents well-marked acid properties. This interesting fact can be illustrated by reference to the derivatives of phenol, C_6H_5OH. This substance, vulgarly known as *carbolic acid*, though capable of exchanging an atom of hydrogen for certain metals is not an acid in the strict sense of the term, and when pure it does not redden litmus. But when treated with chlorine or bromine it yields a succession of compounds in which the acid character is gradually developed in proportion as more of the halogen is exchanged for chlorine. The formulæ of these compounds is represented below :—



$C_6H_4Cl.OH$	$C_6H_4Br.OH$
$C_6H_3Cl_2.OH$	$C_6H_3Br_2.OH$
$C_6H_2Cl_3.OH$	$C_6H_2Br_3.OH$
$C_6Cl_5.OH$	$C_6Br_5.OH.$

They behave as monobasic acids, exchanging one atom of hydrogen for metals.

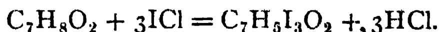
This oxygenic[1] tendency of the halogens is also indicated

[1] Oxygenic = acid producing.

by the destruction of basic character in the amines or compound ammonias by the substitution of chlorine, bromine, or iodine for their hydrogen, as is well shown by the chlorinated derivatives of aniline.

Aniline, C_6H_7N, a powerful base.
Chloraniline, C_6H_6ClN, less basic than aniline.
Dichloraniline, $C_6H_5Cl_2N$, feeble base.
Trichloraniline, $C_6H_4Cl_3N$, neutral.

Iodine.—Iodine presents one or two peculiarities which deserve special notice, as they serve to remove it to some slight extent from immediate association with the kindred elements, bromine and chlorine. In the first place, its affinity for hydrogen is decidedly less energetic than that of either of the other two elements. This is indicated first by the fact that iodine does not usually bleach vegetable colours; secondly, that, acting alone, it is incapable of producing substitution derivatives from carbon compounds.[1] Whenever substitution of chlorine, bromine, or iodine occurs, the hydrogen which is necessarily eliminated goes to form the corresponding hydracid. Now, in the case of iodo-substitution compounds, it has been shown that they are all decomposed by the action of hydriodic acid, with reproduction of the original body and free iodine. Hence iodo-substitution compounds cannot be formed by the action of iodine, unless precautions are taken to remove or to destroy the hydrogen iodide that may be produced. This is effected in various ways, usually by the action of mercuric oxide or iodic acid. The difficulty may also be got over in some instances by substituting iodine monochloride for iodine. Thus, orcinol acted upon by a solution of iodine chloride gives tri-iodorcinol and hydrogen chloride—



$$C_7H_8O_2 + 3ICl = C_7H_5I_3O_2 + 3HCl.$$

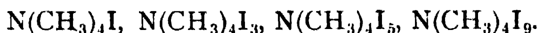
Another distinguishing characteristic of iodine is the

[1] See also Chapter XVIII., Heat of Combination of Iodine with Hydrogen.

intense colour exhibited by the vapour of the element itself, by its solutions in certain liquids, notably in carbon disulphide, by its compound with starch, and by many iodides, the corresponding chlorides or bromides being either colourless or very pale.

In some cases the colour is only observable when the compound is in the solid state. Scarlet mercuric iodide, for example, gives a colourless solution in ether, and yellow lead iodide forms a colourless solution in water. It is probable, therefore, that the colour is due to some peculiarity of crystalline structure in these cases.

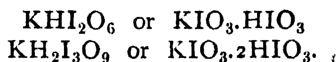
Again, chlorine and bromine are more soluble in water than iodine, and are even capable of forming at low temperatures crystalline hydrates, having the formulæ $Cl_2.10H_2O$ and $Br_2.10H_2O$, no such compound being formed by iodine. On the other hand, the solubility of chlorine and bromine is not increased by the addition of a chloride or bromide to the water in which they are to be dissolved. The solubility of chlorine in aqueous solutions of chlorides is usually less than its solubility in pure water. Iodine, however, is freely soluble in iodide of potassium, and, indeed, produces in this way a black liquid which contains an unstable tri-iodide of potassium, KI_3. This compound forms dark blue deliquescent prisms. The corresponding ammonium salt, NH_4I_3, resembles it closely, and analogous periodides are formed by the ammonium bases, some of which form crystals of great beauty, containing two, four, six, or even eight atoms of iodine in addition to the elements of the normal iodide; as, for example, the following compounds derived from tetramethyl-ammonium iodide:—



$$N(CH_3)_4I,\ N(CH_3)_4I_3,\ N(CH_3)_4I_5,\ N(CH_3)_4I_9.$$

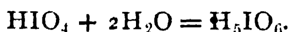
The iodates exhibit some anomalies for which there is no parallel among the chlorates. Thus, in addition to the normal potassic iodate, KIO_3, or $K_nI_nO_{3n}$, there are two other well-crystallised salts for which it is difficult to find

analogues. Their composition may be expressed alternatively as follows:—



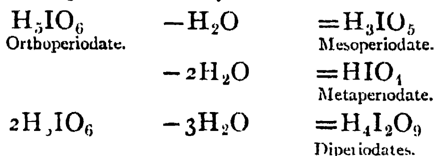
$$KHI_2O_6 \text{ or } KIO_3.HIO_3$$
$$KH_2I_3O_9 \text{ or } KIO_3.2HIO_3.$$

Periodic acid is still more anomalous, for it yields salts such as $Na_2H_3IO_6$, which show that the hydrogen in the molecule is divisible into five parts; hence the formula of the acid is not simply HIO_4, corresponding to chloric acid, $HClO_4$, but must include the elements of water



$$HIO_4 + 2H_2O = H_5IO_6.$$

These may be regarded as orthoperiodates and from them, by removal of the elements of water or metallic oxide, other classes of periodates may be obtained



H_5IO_6 Orthoperiodate.	$-H_2O$	$=H_3IO_5$ Mesoperiodate.
	$-2H_2O$	$=HIO_4$ Metaperiodate.
$2H_5IO_6$	$-3H_2O$	$=H_4I_2O_9$ Diperiodates.

Fluorine.—This element has been at last isolated (1886) by the electrolysis of a mixture of hydrogen and potassium fluorides. It is a pale yellow gas which decomposes water, forming hydrogen fluoride and ozone. The liquid element boils at about $-187°$. Silicon and boron burn in the gas, forming fluorides. Fluorine is separated from the other halogens, partly by its extraordinary attraction for silicon, partly by the non-existence of any oxide or oxyacid of fluorine. In spite, also, of their general resemblance to the chlorides, bromides, and iodides, individual fluorides differ in many cases from the corresponding chlorides. Thus, fluoride of calcium is insoluble, chloride of calcium very soluble and deliquescent; fluoride of silver is soluble in water, chloride of silver totally insoluble; fluoride of potassium soluble in water, but, unlike the neutral stable chloride, it yields an alkaline solution which probably con-

tains caustic potash and the double hydrogen and potassium fluoride.



$$2KF + OH_2 = KOH + KF.HF.$$

The tendency to produce double salts of this kind has, indeed, led to the idea that fluorine may be really a bivalent element, like oxygen, with the atomic weight 38. The formula of the double fluorides would then be comparable with those of oxygen compounds.

Fluorides		Oxides
H_2F	analogous to	H_2O
KHF	,,	KHO
KBF_2	,,	KBO_2
K_2SiF_3	,,	K_2SiO_3
K_2SnF_3	,,	K_2SnO_3
&c.		&c.

There cannot, however, be any doubt that the molecule of gaseous hydrogen fluoride is constituted similarly to gaseous hydrogen chloride, and must be represented by the formula HF, notwithstanding its disposition to associate into more complex molecules H_nF_n (where n is greater than 1) at temperatures from the boiling point 19°·4, up to near 88° when the density becomes normal and constant.

The double fluorides moreover are not more numerous or prominent than are the double chlorides, bromides, and iodides, and it seems not unreasonable to explain their existence by a similar hypothesis. The atom F (= 19) is probably trivalent. If so, the constitution of fluoride of potassium and hydrogen may be represented as



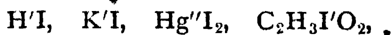
$$KF = FH,$$

and that of the other fluorides, single and double, in a similar manner.

Valency of the Halogens.—An atom of a halogen never replaces, in a direct manner, more than one atom of hydrogen. In the haloid salts of these elements, 35·45 parts of

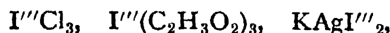
chlorine and equivalent quantities of bromine, iodine, and fluorine are almost always combined with the metallic representative of one part by weight of hydrogen. The halogens are therefore generally univalent. Nevertheless, many compounds are known, the existence of which can scarcely be accounted for except upon the hypothesis that they are occasionally trivalent.

Thus, in addition to the normal iodides and iodo-substitution compounds,



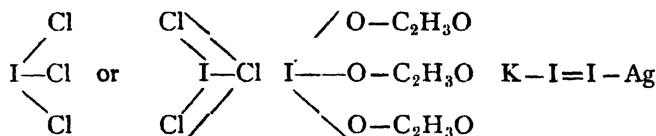
$$H'I, \quad K'I, \quad Hg''I_2, \quad C_2H_3I'O_2,$$

iodine forms the following compounds:



$$I'''Cl_3, \quad I'''(C_2H_3O_2)_3, \quad KAgI'''_2,$$

which may be written as follows:



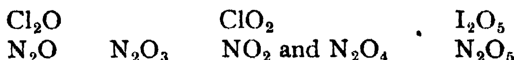
In some of their oxygenated compounds, chlorine, bromine, and iodine present also a resemblance to nitrogen, which is most usually a triad. Thus we have agreement in the empirical formulæ of hypochlorous and hyponitrous acids, chlorous and nitrous acids, chloric and nitric acids.



$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
HNO	HNO_2	HNO_3	

The nitrogen analogue of perchloric acid is at present unknown.

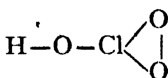
A further correspondence is observable in their oxides:



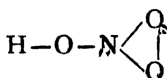
Cl_2O		ClO_2	I_2O_5
N_2O	N_2O_3	NO_2 and N_2O_4	N_2O_5

Now, if we admit that nitrogen is trivalent in these compounds, the presumption that chlorine and its congeners

are also trivalent is, at least, worthy of discussion. The following graphic formulæ express the constitution of chloric and nitric acids upon this hypothesis :—



Chloric acid.



Nitric acid.

A further comparison between iodine and nitrogen may be traced in the formation by the former element, though not by chlorine or bromine, of compounds which correspond in composition and to some extent also in properties with the nitroso- and nitro- derivatives of many carbon compounds. Iodosobenzene C_6H_5IO, for example, is comparable with nitrosobenzene C_6H_5NO, and iodoxybenzene $C_6H_5IO_2$ with nitrobenzene $C_6H_5NO_2$. Further, iodine is even capable of simulating the character of nitrogen in producing compounds of a basic character similar to that of the compound ammonium bases.

Diphenyl-iodonium hydroxide $(C_6H_5)_2I.OH$, for instance, is a strongly alkaline substance which absorbs carbon dioxide, and forms crystalline salts by exchanging hydroxyl, OH, for acid radicles, *e.g.* the chloride $(C_6H_5)_2I.Cl$.

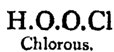
In making such a comparison, however, it is important to avoid the errors that may be involved in the use of the simplest or non-molecular formulæ. Thus hyponitrous acid, or hydrogen hyponitrite, is not known, but there is strong evidence, derived from the properties of some of its salts and from certain modes of its formation, that the true molecular formula would be $H_2N_2O_2$ and not simply HNO. With regard to the constitution of the oxyacids of chlorine, it must be remembered that perchloric acid, although it contains more oxygen than chloric acid, is far more stable. Hence probably these two compounds are differently constituted, and while chloric acid and the two lower acids may be assumed to possess one type of structure, perchloric

acid almost certainly presents another. Supposing chlorine uniformly monad the three lower acids must be represented by the following formulæ :—



$$H.O.Cl$$

Hypochlorous.



$$H.O.O.Cl$$

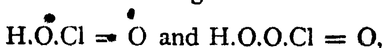
Chlorous.



$$H.O.O.O.Cl$$

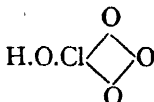
Chloric.

If chlorine be assumed to be trivalent the formulæ for chlorous and chloric acids might be



$$H.O.Cl = O \text{ and } H.O.O.Cl = O,$$

while perchloric acid on the same assumption may be represented by a formula in which the oxygen atoms are united so as to form a closed ring, thus,



For such an expression there is only indirect evidence based on the observation that among carbon compounds superior stability is commonly attributed to the formation of a somewhat similar ring. There is, however, no method at present known by which the constitution of such compounds as perchloric acid can be investigated.

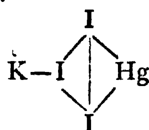
Chlorine is sometimes supposed to be septivalent or heptad, but the discussion of this hypothesis must be reserved for the present (see MANGANESE).

As contributing evidence that all the halogens have a reserve of combining capacity over and above that which is manifested in the simplest compounds HCl, KBr, CH_3I, &c., we might also point to the large number of permanent and definite double compounds which the chlorides, bromides, and iodides are capable of forming. We have, for example, the well-known chloro-platinates of the alkali metals—



$$2NaCl.PtCl_4$$
$$2KCl.PtCl_4, \&c.,$$

besides the innumerable compounds of the alkali-metal chlorides with the chlorides of magnesium, iron, aluminium, mercury, copper, and other metals. Although a few of these compounds are decomposed by water, the majority of them are stable enough, and give no signs of alteration by such treatment. Their constitution is most reasonably represented upon the assumption of the trivalence of the halogen. The compound $KI.HgI_2$, for example, may be written in this manner :

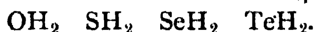


Some chemists regard these compounds as formed by the union of entire molecules of the constituent salts, combined together by some kind of adhesion differing from ordinary chemical affinity. Thus the potassio-mercuric iodide represented above is considered to contain both iodide of potassium and iodide of mercury, $HgI_2 + KI$. This salt, however, is colourless, soluble in water, and totally unlike the scarlet insoluble mercuric iodide, the elements of which it contains, and, so far as physical characters are concerned, there is nothing to distinguish such cases from examples of ordinary atomic combination.

NON-METALS.—GROUP 2.

	Symbols.	Atomic Weights.	
Oxygen . .	O	= 16	
Sulphur . .	S	= 32·06	S + Te = 79·53.
Selenion . .	Se	= 79·10	
Tellurium . .	Te	= 127	

These elements are associated together principally by reason of the correspondence in composition and general properties among their compounds with hydrogen—



$$OH_2 \quad SH_2 \quad SeH_2 \quad TeH_2.$$

For although, taking any two adjacent terms of the series, many points of resemblance may be traced out, yet there is a very wide interval between the colourless gas oxygen and the silvery, metallic, crystalline solid tellurium.

Oxygen, standing apart from the rest in virtue of many extraordinary qualities, deserves to be noticed first. This element constitutes nearly one-half the total weight of the earth's crust. Indeed, it seems to be the preponderating element of the globe. Leaving out of account the insignificant quantities of metals and metallic sulphides embedded in the earth, it may be said that the entire constituents of the earth's crust, including the water of the ocean, consist of compounds saturated with oxygen ; and even supposing all organic bodies to be completely burnt up, the atmosphere would still contain a considerable quantity of unemployed oxygen.

Oxygen is entirely unmatched among the rest of the elements, both as regards the number and varied character of its compounds, and the important part which it plays in relation to combustion and life.

Water, hydrogen protoxide, also exhibits properties which are in every way remarkable as specially fitting it for the part it has to play in the economy of nature—the very type of a neutral body, yet capable, under special circumstances, of acting either as a feeble base or a feeble acid ; an almost universal solvent of saline bodies ; exhibiting the anomaly of attaining maximum density at a temperature (4°) above its solidifying point ; standing alone amongst liquids by reason of its great capacity for heat ; having a vapour-density little more than half that of its gaseous sulphur analogue (SH_2), and yet liquefying and solidifying readily.

The higher oxide of hydrogen, O_2H_2, with its bleaching and oxidising powers, resembles in no slight measure the element chlorine.

The name *oxygen*, 'acid producer,' from ὀξύς and γεννάω, was given by Lavoisier under the mistaken impres-

sion that this element contained a principle common to all acids. This we know was an error. Nevertheless, the name was not ill-chosen, and for the following reasons :—

1. The majority of known acids contain oxygen. The chief exceptions to this statement are as follows :—

(*a*) The so-called hydracids, HF, HCl, HBr, HI, HCN, and their compounds, such as fluoboric acid, $HF.BF_3$ or HBF_4, fluosilicic acid, $2HF.SiF_4$ or H_2SiF_6, chlorauric and chloroplatinic acids, $HCl.AuCl_3$ or $HAuCl_4$, $2HCl.PtCl_4$ or H_2PtCl_6, &c.

(*b*) Thio-acids, which may be regarded as oxygen acids, a part or the whole of the oxygen of which is replaced by sulphur, *e.g.*—

Thiosulphuric acid . . .	H_2SO_3S
Thiocarbonic acid . . .	H_2CS_3
Thiacetic acid . . .	HC_2H_3OS

2. In proportion as the quantity of oxygen increases in a series of acids containing the same elements, so the acidity as well as the stability of the compound is almost always increased. A detailed examination of such examples as the following would, if space permitted, confirm this statement:

$HClO$	HNO_2	H_2SO_3	H_3PO_2
$HClO_2$	HNO_3	H_2SO_4	H_3PO_3
$HClO_3$			H_3PO_4
$HClO_4$			

Glycolic acid, $C_2H_4O_3$
Oxalic acid, $C_2H_2O_4$

3. The addition of oxygen to (neutral) aldehyds converts them into acids. *Ex. gr.*—

Acetic.	
Aldehyd	C_2H_4O
Acid	$C_2H_4O_2$
Benzoic.	
Aldehyd	C_7H_6O
Acid	$C_7H_6O_2$

4. In homologous series of acids, the lowest terms which are richest in oxygen show a far stronger development of the acid character than the higher terms of the same series, which are comparatively poor in oxygen. Compare, for example—

Formic acid, CH_2O_2,	containing	69·5	per cent.	of oxygen,
Acetic acid, $C_2H_4O_2$	„	53·3	„	„
with				
Valeric acid, $C_5H_{10}O_2$	„	31·3	„	„
and				
Palmitic acid, $C_{16}H_{32}O_2$	„	12·4	„	„

5. Many oxides of metals are basic, that is, saturate acids with production of water and salt, but a few examples will be sufficient to show that it is only those which contain a comparatively small quantity of oxygen that possess this power. As the quantity of oxygen increases in a given series, the basic character gradually disappears, and gives place to a more or less decided acid-forming tendency.

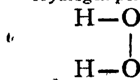
EXAMPLES OF METALLIC OXIDES.

Basic	Hg_2O HgO	K_2O	BaO	PbO	MnO Mn_2O_3 (feebly)	CrO Cr_2O_3(feebly)
Intermediate		K_2O_2 K_2O_4	BaO_2	PbO_2	MnO_2	
Acidic					MnO_3 Mn_2O_7	CrO_3

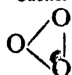
Allotropic oxygen or *ozone* is a body which has attracted considerable attention. The experiments of Brodie finally decided the question of its constitution in favour of the hypothesis long ago put forward by Odling. Ozone is now proved to be allotropic oxygen, free from hydrogen, and to have the formula O_3. It may thus be regarded as formed

on the type of hydrogen peroxide, with which body it agrees in many of its reactions.

Hydrogen peroxide.



Ozone.



Sulphur, Selenion.—These two elements resemble each other closely. Sulphur is a yellow, selenion a red solid, exhibiting several modifications, some of which are crystalline and soluble in carbon disulphide, others amorphous and insoluble.

Principal Allotropes of Sulphur.

	Rel. Dens.	In carbon disulphide.
1. Octahedral (native) .	2·07	soluble.
2. Prismatic (monoclinic) .	1·98	transformed into 1.
3. Plastic	1·95	insoluble.
4. Amorphous . . .	1·95	insoluble.

(Precipitated from sulphur chloride or from thiosulphates.)

Principal Allotropes of Selenion.

1. Monoclinic (native) .	4·4	soluble.
2. Crystalline (form ?) .	4·8	insoluble.
3. Vitreous . . .	4·3	insoluble.
4. Amorphous . . .	?	insoluble.

(Precipitated from selenious acid.)

The following is a comparison of the most important compounds of sulphur and selenion :—

H_2S Gas.	SO_2 Gas.	SO_3 Solid.	H_2SO_3 Crystallisable as hydrate at low temperatures.	H_2SO_4 Dense crystallisable liquid.
H_2Se Gas.	SeO_2 Solid.	SeO_3 Unknown.	H_2SeO_3 rystalline solid.	H_2SeO_4 Dense crystallisal liquid.

The selenates are isomorphous with the sulphates.

The relations of sulphur to oxygen are shown in the following synopsis of some of their compounds :—

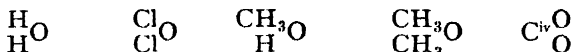
SULPHUR.	OXYGEN.
SH_2 gas, feebly acid S_2H_2 oily liquid CS colourless gas ? CS_2 volatile liquid COS gas	OH_2 O_2H_2 oily liquid CO colourless gas CO_2 gas
ACIDS.	
$C_2H_3O.SH$ thiacetic. B.P. 93° $SO_2.OH.SH$ thiosulphuric	$C_2H_3O.OH$ acetic. B.P. 120° $SO_2.OH.OH$ sulphuric
BASIC.	
Sulphides.	*Oxides.*
SKH SK_2 SCa $CS(NH_2)_2$ thiocarbamide	OKH OK_2 OCa $CO(NH_2)_2$ carbamide or urea
SALTS.	
M'_2CS_3 thiocarbonate M'_3AsS_4 thioarsenate M'CNS thiocyanate	M'_2CO_3 carbonate M'_3AsO_4 arsenate M'CNO cyanate
ALCOHOLS.	
$S\left\{\begin{matrix}C_2H_5\\H\end{matrix}\right.$ mercaptan. B.P. 36°	$O\left\{\begin{matrix}C_2H_5\\H\end{matrix}\right.$ B.P. 78°·4
ETHERS.	
$S(C_2H_5)_2$. B.P. 72°	$O(C_2H_5)_2$. B.P. 35°·6

It is necessary, however, to add that many oxygen compounds are known for which at present there are no corresponding terms in the sulphur series—the oxides of nitrogen, for example. On the other hand, sulphur has a power of accumulating in a manner which is not exhibited, at least

to the same extent, by oxygen. Consequently, many polysulphides exist for which there are no corresponding oxides. Thus we have K_2S_5, CaS_5, FeS_2, $(C_2H_5)_2S_2$, and $(C_2H_5)_2S_3$.

Valency of Oxygen and Sulphur.

Oxygen is generally diad or bivalent, and in its gaseous or vaporisable compounds, with one exception, it is invariably so. Thus each of the formulæ following represents the normal two volumes of vapour :—

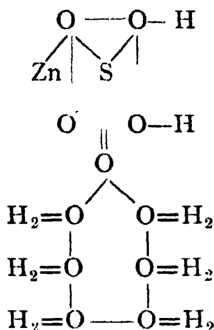


Carbonic oxide is usually represented as containing unsaturated carbon, C:O, but, as will be shown, there are some reasons for believing that oxygen is essentially tetrad, though in such cases as those referred to above only one half its valence is actually called into use. On the hypothesis that oxygen is quadrivalent in carbonic oxide, the formula may be written C:O.

The quadrivalent character of oxygen has been partly based upon the supposed existence of lower oxides of copper and silver, Cu_4O and Ag_4O, but the evidence concerning the composition of these substances is unsatisfactory. The existence of compounds such as the products of the union of methyloxide with hydrogen chloride, $(CH_3)_2O.HCl$ and methyl chloride with water $CH_3Cl.H_2O$ can only be explained by supposing that the molecules are united by the residual valency of the oxygen and chlorine. There are other compounds, the composition of which necessitates the assumption that the oxygen in them is also quadrivalent, but unfortunately their composition is somewhat complex, and is unsuitable for discussion in a comparatively elementary book.

Water of crystallisation is often considered by chemists

to exist as water in the salts in which it occurs, the molecules of the salt and the molecules of the water retaining their individuality, being united only by some kind of adhesion. Such water is very easily detached, and constitutes no essential part of the chemically reacting unit of the compound in all the most characteristic of its transformations. Nevertheless, the idea that this water is held to the salt by the two extra units of combining power of the oxygen is far more probable. One example of the application of this hypothesis will suffice. Zinc sulphate contains $ZnSO_4.7OH_2$, or $ZnSO_4OH_2.6OH_2$. This may be expressed in the following manner:—



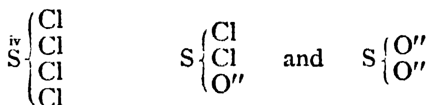
Now it is well known that six out of the seven molecules of water present in crystals of zinc sulphate are expelled by heat much more readily than the last molecule, which can be detached only with great difficulty. This fact is recorded in the second of the two formulæ given above, and it also comes out in the graphic formula in which two atoms of hydrogen are represented as occupying a position in the molecule corresponding with that of the zinc.

Another fact which deserves to be noted is that oxygen is nearly related to sulphur, as already shown, and though the capacity for combination is more fully developed in

the latter element than in oxygen, it is probable that a part of the valency of oxygen, ordinarily latent, may under certain circumstances be called into play. In addition to the facts concerning sulphur already mentioned, the student may be reminded that while oxygen has a normal density 16, approximately, down to very low temperatures, the density of sulphur vapour, many degrees above its boiling point, shows that the molecules are more complex than those of oxygen, and it only becomes nearly equal to the atomic weight at a red heat, or from 800° to 1,000°.

With regard to sulphur the question is somewhat different. This element forms three well-marked classes of compounds. In the first of these it is bivalent, and may be regarded as the strict representative of oxygen. Examples of this type of compound have been already given, SH_2, S_2H_2, CS_2, COS.

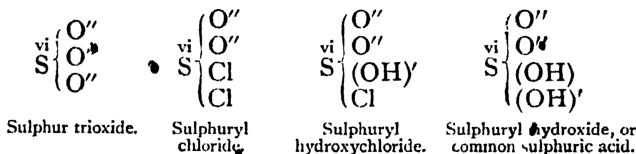
In the second class the sulphur alone is quadrivalent: *ex. gr.* in—



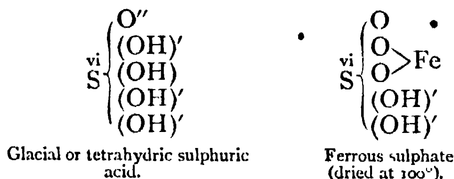
Sulphur tetrachloride. Thionyl chloride. Sulphur dioxide.

In the third class of sulphur compounds, represented by sulphur trioxide, SO_3, the central atom seems to be sexivalent sulphur: $\begin{matrix} O \\ \| \\ O{=}S{=}O \end{matrix}$. It is true that the constitution of this and all the rest of the sulphur compounds might be represented on the hypothesis that sulphur is diad, $\begin{matrix} O—S—O \\ \diagdown \quad \diagup \\ O \end{matrix}$, but the analogy of sulphur with chromium, and especially the isomorphism of the sulphates and chromates, seem to establish the title of sulphur to be regarded as a hexad.

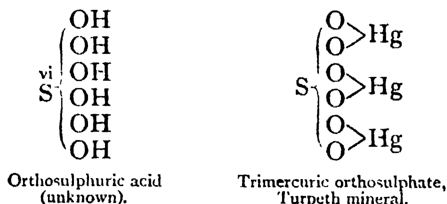
The several oxides, hydroxides, and oxychlorides are therefore represented in the following manner :—



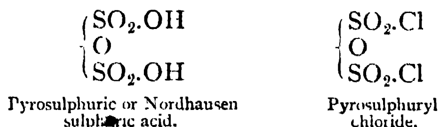
Sulphur trioxide. Sulphuryl chloride. Sulphuryl hydroxychloride. Sulphuryl hydroxide, or common sulphuric acid.



Glacial or tetrahydric sulphuric acid. Ferrous sulphate (dried at 100°).



Orthosulphuric acid (unknown). Trimercuric orthosulphate, Turpeth mineral.



Pyrosulphuric or Nordhausen sulphuric acid. Pyrosulphuryl chloride.

NON-METALS.—GROUP 3 : BORON.

A triad element, but exhibiting marked analogies with tetrad silicon. The following are their chief points of agreement :—

BORON.	SILICON.
Element, (*a*) amorphous brown powder or (*b*) quadratic octahedrons.	Element, (*a*) amorphous brown powder or (*b*) hexagonal plates
Density 2·68	Density about 2·5
BH_3 inflammable gas	SiH_4 spontaneously inflammable gas
$B(CH_3)_3$, $B(C_2H_5)_3$, &c.	$Si(CH_3)_4$, $Si(C_2H_5)_4$, &c.
BCl_3. B.P. 17°	$SiCl_4$. B.P. 59°
BF_3 gas	SiF_4 gas
$BF_3.HF$ or BHF_4 known only in solution: salts crystallisable	$SiF_4.2HF$ or SiH_2F_6 scarcely known except in solution; salts tolerably stable
H_3BO_3 crystallisable	H_4SiO_4 exists only in solution
HBO_2	H_2SiO_3
B_2O_3 (fused, Dens. 1·83)	SiO_2 (fused, Dens. 2·2)
M'_3BO_3 orthoborates	M'_4SiO_4 orthosilicates
$M'BO_2$ metaborates	M'_2SiO_3 metasilicates
Anhydroborates, $M'BO_2 + xB_2O_3$	Anhydrosilicates, $M'_2SiO_3 + xSiO_2$
Example, fused borax, $2NaBO_2 + B_2O_3$	Example orthoclase felspar $\left.\begin{matrix}K_2SiO_3\\ Al_2(SiO_3)_3\end{matrix}\right\} + 2SiO_2$

Boric acid is a feeble acid and is readily distinguished from such acids as sulphuric acid by its action on vegetable colours. It is volatile in the vapour of water and alcohol, and may be distilled in considerable quantity with these liquids. On the other hand the trioxide, which is left when boric acid is dehydrated by heat, is vaporisable only at a white heat. It is therefore capable of displacing the elements of the corresponding acidic oxide when fused with many salts: sulphates, nitrates, carbonates are thus decomposed with expulsion of sulphur trioxide, nitrogen pentoxide, and carbon dioxide respectively. It is, however, worthy of note that boron trioxide is capable of exhibiting a feebly basic character, as it forms unstable compounds with sulphuric and phosphoric oxides, and it produces a tartrate, $K(BO)C_4H_4O_6$, corresponding in composition to tartar

emetic (*see* Arsenic and Antimony). It also appears to play in some minerals a part similar to that taken by alumina, Al_2O_3.

Boron combines directly with nitrogen forming a compound, BN or perhaps B_3N_3, which can also be produced by heating together ammonium chloride and anhydrous borax.

NON-METALS.—GROUP 4.

Carbon, C = 12.
Silicon, Si = 28·4.

Allotropes of Carbon.

a. Diamond, octahedral, Dens. 3·3 to 3·5.
b. Graphite, hexagonal, Dens. about 2·2.
c. Charcoal, amorphous.

Allotropes of Silicon.

a. Adamantine (?).
b. Graphitic, hexagonal, Dens. about 2·5.
c. Amorphous.

Carbon is remarkable as being the essential element of organic nature, and silicon as being one of the most abundant constituents of the earth's solid crust. Regarded as chemical elements, they present problems of special interest in the multitudinous array of compounds which they have furnished to the chemist. The carbon compounds will be specially considered hereafter; it therefore only remains to point out in this place a few of the coincidences of composition so frequently observed between the compounds of these two elements.

In comparing carbon and silicon compounds together, it

cannot be said that the similarity so often noticed in their constitution extends to their properties. In most cases corresponding carbon and silicon compounds are very different bodies. A few examples only can be referred to:

Carbon Compounds.	Silicon Compounds.
CO, colourless inflammable gas.	SiO, unknown.
CO_2, colourless gas, soluble to some extent in water.	SiO_2, crystalline solid, fusible only at a very high temperature, totally insoluble in water. Hydrates slightly soluble.
CH_4, permanent gas.	SiH_4, spontaneously inflammable gas.
$CHCl_3$, heavy liquid, unacted upon by water.	$SiHCl_3$, liquid, decomposed by water.

Orthosilicic and orthocarbonic acids, H_4SiO_4 and H_4CO_4, are unknown, and but very few of their compounds have been studied. Of orthosilicates we have olivine, Mg''_2SiO_4, ferrous orthosilicate, Fe''_2SiO_4, the ethylic ester, $(C_2H_5)_4SiO_4$, and a few others. Orthocarbonates are represented by such compounds as the ammonium-hydrogen orthocarbonate $(NH_4)_2H_2CO_4$, and the ester $(C_2H_5)_4CO_4$. Ordinary carbonates are derived from metacarbonic acid, H_2CO_3, a body which has not been isolated, though the corresponding silicic acid has been obtained as a solid glassy mass. All carbonates are decomposed on the addition of even the weakest acids, whereas the majority of the silicates are attacked but very slowly by acids. Nevertheless silicates containing alkaline or earthy oxides are slowly decomposed even by carbonic acid, which extracts the alkali, leaving hydrated silica, alumina and ferric oxide, &c.

Silicon is capable of forming a number of compounds in which it appears to simulate the habit of carbon and to be capable of replacing it, atom for atom, to a greater or less extent. The formulæ of few of these compounds are

tabulated below together with those of their carbon prototypes :

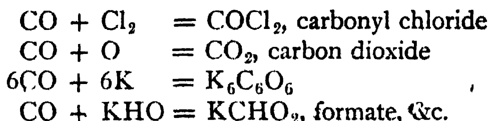
Formic acid.	Silicoformic acid.
$HCO.OH$	$HSiO.OH$
Propionic acid.	Silicopropionic acid.
$C_2H_5.CO.OH$	$C_2H_5.SiO.OH$
Benzoic acid.	Silicobenzoic acid.
$C_6H_5.CO.OH$	$C_6H_5.SiO.OH$
Tetraphenylmethane.	Tetraphenylsilicomethane.
$C(C_6H_5)_4$	$Si(C_6H_5)_4$
Ethylic orthocarbonate.	Ethylic orthosilicate.
$C(OC_2H_5)_4$	$Si(OC_2H_5)_4$

The significance of these facts, however, is perhaps not so great as appears at first sight, for the properties of the two classes of compounds are usually very different, and boron, which is *trivalent*, is capable of playing the same part as the silicon in the compounds referred to. Boron trimethide $B(CH_3)_3$, a gas, for example, and boron triethide $B(C_2H_5)_3$, a very volatile liquid, are compounds in which the boron atom links together three carbon atoms in the same way that an atom of carbon unites four atoms in tetramethylmethane, $C(CH_3)_4$ a liquid of boiling point is about 10°. Both the silicon and the boron compounds in which these elements are directly combined with carbon, and which contain no oxygen, are distinguished from the corresponding compounds in which carbon alone occurs by the readiness with which they absorb oxygen.

Valency of Carbon and Silicon.

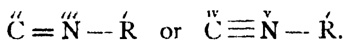
Silicon is always tetrad. Carbon is tetrad in all its known compounds, except possibly carbonic oxide, CO, and the isocyanides (see p. 120). The unsaturated character of carbonic oxide is shown by the readiness with which it enters into combination with chlorine, with oxygen, with

potassium, with caustic potash, and with cuprous or platinous chloride.



$$
\begin{aligned}
CO + Cl_2 &= COCl_2, \text{ carbonyl chloride} \\
CO + O &= CO_2, \text{ carbon dioxide} \\
6CO + 6K &= K_6C_6O_6 \\
CO + KHO &= KCHO_2, \text{ formate, \&c.}
\end{aligned}
$$

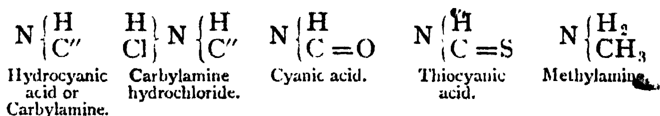
From the characteristic reactions of the isocyanides (see p. 120) it appears that in these compounds an atom of carbon is linked to the hydrogen, or other positive radicle present, by the atom of nitrogen. Now, according as we regard the nitrogen in these compounds as discharging a triad or pentad function, we must attribute to the carbon a replacing value equal to two or four atoms of hydrogen. Either of these two formulæ, then, may be adopted :—



$$\overset{\prime\prime}{C} = \overset{\prime\prime\prime}{N} - \overset{\prime}{R} \quad \text{or} \quad \overset{\text{iv}}{C} \equiv \overset{\text{v}}{N} - \overset{\prime}{R}.$$

The one may be regarded as a derivative of ammonia, the other of marsh-gas.

In favour of the former view we may adduce the combination of such a cyanide as prussic acid with hydrochloric, hydrobromic, and hydriodic acids, forming crystalline compounds analogous to sal-ammoniac, and with hydrogen forming methylamine ; also the combination of the isocyanides generally with oxygen to form isocyanates, and with sulphur to form isothiocyanates. These combinations may be represented thus :—



$N\begin{cases}H \\ C''\end{cases}$ Hydrocyanic acid or Carbylamine.

$\begin{matrix}H \\ Cl\end{matrix}\Big\} N\begin{cases}H \\ C''\end{cases}$ Carbylamine hydrochloride.

$N\begin{cases}H \\ C=O\end{cases}$ Cyanic acid.

$N\begin{cases}H \\ C=S\end{cases}$ Thiocyanic acid.

$N\begin{cases}H_2 \\ CH_3\end{cases}$ Methylamine.

If the second hypothesis is adopted, we must imagine that the union of the carbon to the nitrogen is partly unlocked before these compounds can be found. Thus the

change from hydrogen cyanide to cyanate, for example, would be expressed as follows :—



Cyanide.



Cyanate.

The formation of the hydrochloride seems to require the assumption that the carbon becomes dyad as shown in the formula given above, unless it is supposed that the elements of hydrogen chloride unite directly with the carbon, which is less probable.

NON-METALS.—GROUP 5 : NITROGEN AND PHOSPHORUS.

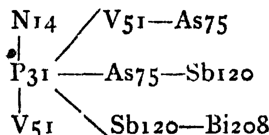
Nitrogen	N	= 14·04	
Phosphorus	P	= 31	$\frac{N + V}{2} = 32·62$
Vanadium	V	= 51·2	

Phosphorus	P	= 31	
Vanadium	V	= 51·2	$\frac{P + As}{2} = 53$
Arsenic	As	= 75	

Phosphorus	P	= 31	
Arsenic	As	= 75	$\frac{P + Sb}{2} = 75·5$
Antimony	Sb	= 120	

Phosphorus	P	= 31	
Antimony	Sb	= 120	$\frac{P + Bi}{2} = 119·75$
Bismuth	Bi	= 208·5	

Diagram of Numerical Relations typical of Chemical Relations.



In this list of elements there is a change, concurrently with the increase of atomic weight, from the obviously non-metallic character, displayed by nitrogen, to a considerable development of the characteristic features of a metal, as

seen in bismuth. Nitrogen and phosphorus are marked off from the rest chiefly by reason of the peculiar properties of their principal compounds with hydrogen, ammonia, NH_3, and phosphine PH_3, and the bases formed from them by substitution of hydrocarbon radicles for hydrogen.[1] Ammonia is distinctly characterised by its power of uniting, directly and as a whole, with all acids without exception. Phosphine imitates ammonia in combining with the hydracids HCl, HBr, HI. The compounds thus formed are, however, dissociated more easily into the base and the acid than are the corresponding compounds of ammonia, for while sal-ammoniac is a perfectly stable crystallisable compound at common air temperatures, phosphonium chloride, PH_4Cl, can exist at such temperatures only under pressure. That phosphine is not known to be capable of uniting with other acids probably arises from the readiness with which the phosphorus in it seizes upon oxygen, so that the sulphate which is said to be formed at low temperatures is decomposed under ordinary conditions, the phosphorus taking oxygen and liberating sulphur and hydrogen sulphide. Ammonia and phosphine, however, are not the only compounds which nitrogen and phosphorus form with hydrogen. The nitrogen series is particularly interesting as seen below:—

NITROGEN COMPOUNDS.	PHOSPHORUS COMPOUNDS.[2]
Diazoimide or Hydrazoic Acid. N_3H	(Unknown.) P_3H
Hydrazine. N_2H_4 Volatile liquid strongly basic.	P_2H_4 Volatile liquid.
NH_3 Gas, very soluble in water, strongly basic.	PH_3 Gas, very slightly soluble in water, feebly basic.

[1] *See* Amines, &c., Chapter XV.

[2] The orange coloured substance supposed to consist of the compound P_2H or P_4H_2 described in books is probably allotropic phosphorus.

The relations of nitrogen and hydrogen respectively in these compounds are very curious. The presence of one atom of hydrogen combined with nitrogen confers on the compound acid properties so long as the other constituents of the molecule are not decidedly positive in character. Thus

$HN:N_2$ is hydrazoic acid
$HN:CO$ is cyanic acid
but
$HN(CH_3)_2$ is dimethylamine, a powerful base.

The addition of a second hydrogen atom to the nitrogen produces a compound with basic properties and tendencies. Thus

$H_2N.NH_2$, H_2NCH_3, $H_2NC_6H_5$, &c.

are bases, and even $(H_2N)_2CO$ acts as a base towards strong acids, although the negative influence of the acidic group CO is felt (*see* Amides).

As regards the properties of nitrogen and phosphorus in the elemental form they present a marked contrast to each other. Nitrogen is a gas liquefiable only at very low temperatures and not known in any allotropic form. Its density agrees with the molecular formula N_2. Although nitrogen at common temperatures and pressures is incombustible, and is not capable of entering very readily into combination with oxygen, it is absorbed very rapidly by several elements, boron, magnesium, and the alkali metals, at a red heat.

Phosphorus, on the other hand, is in its ordinary condition a crystalline though easily fusible and volatile solid, with a vapour density which corresponds with the formula P_4. It is also capable of passing into several allotropic modifications, and is distinguished by the readiness with which it unites with oxygen, sulphur, chlorine, &c. The oxides and acids of nitrogen in their volatility and easy decomposability, form a strong contrast to the corresponding

compounds of phosphorus. The accident of agreement in their crude or synoptic formulæ by no means implies identity of constitution, and it seems probable that the atomic structure of the nitrogen oxides and acids is, at least in many cases, different from that of the phosphorus compounds.

The following are examples of agreement in the crude or empirical formulæ of compounds of nitrogen and of phosphorus with oxygen :—

Trioxides.	Tetroxides	Pentoxides.	Acids.
N_2O_3	N_2O_4	N_2O_5	HNO_3
P_2O_3	P_2O_4	P_2O_5	HPO_3

But this apparent concordance is deceptive, for the molecular weight of the phosphorus compounds must be expressed by double these formulæ, namely—

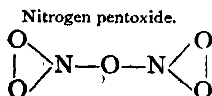


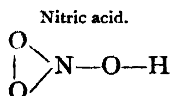
P_4O_6 P_4O_8 P_4O_{10} $H_2P_2O_6$

The vapour densities of all these compounds, except P_4O_8, have been experimentally determined, and there is no reason for attributing a different structure to this intermediate oxide, which is very similar in general properties to the other two.

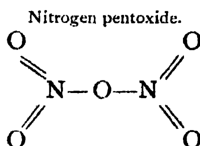
The compounds N_2O, NO, HNO_2, find no parallels in the phosphorus series, while H_3PO_4, H_3PO_3, H_3PO_2, $H_4P_2O_7$, the salts of which, at least, are highly stable and definite, are altogether unrepresented among the nitrogen compounds. Again, while phosphorus yields two chlorides, PCl_3 and PCl_5, and an oxychloride, $POCl_3$, nitrogen forms one chloride, NCl_3, and an oxychloride, $NOCl$, a yellow gas. It has been the very general custom to represent all the compounds of nitrogen by formulæ framed in the same manner as those of the phosphoric compounds, without regard to their dissimilar properties. But by assuming that nitrogen is trivalent in these bodies we render some account of these discrepancies. On this view the formulæ given

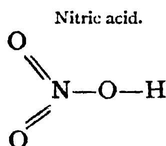
above for nitric acid and nitrogen pentoxide may be expanded in the following manner[1] :—


Nitrogen pentoxide.


Nitric acid.

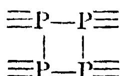
It is, however, possible that in these compounds the nitrogen may be pentad, as it appears to be in ammonium salts (p. 255). Nitric acid and its anhydride would then be expressed as follows :—


Nitrogen pentoxide.


Nitric acid.

The difference between these compounds and the oxides and acids of phosphorus in respect to volatility and perhaps other characters would then be accounted for, at least partly, by the lower molecular weight and simpler structure of the nitrogen compounds.

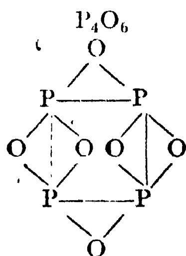
The group of four atoms which constitutes the molecule of phosphorus is a very stable structure which bears very high furnace temperatures without showing signs of breaking up. Supposing this molecule to be constituted in the manner represented by this formula :—

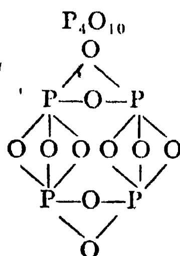


it is obvious that there are but twelve units of valency

[1] The formulæ might also be written O = N – O – O – O – N = O, and O = N – O – O – H, though for several reasons the form given in the text is preferable.

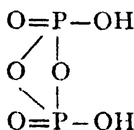
disposable. Hence to account for the addition of ten atoms of oxygen we must assume either that atoms of oxygen are inked together or that the union between the atoms of phosphorus is broken in the highest oxide. The following seem to be the most probable formulæ :—



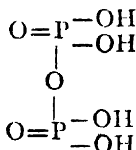


On the addition of water to phosphoric oxide the molecule is divided into two parts and metaphosphoric acid results. From this the usual formulæ for pyrophosphoric acid and orthophosphoric acid, the successive products of the addition of water, are easily deduced.

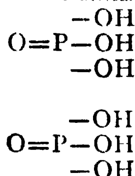
Metaphosphoric.



Pyrophosphoric.



Orthophosphoric two molecules.



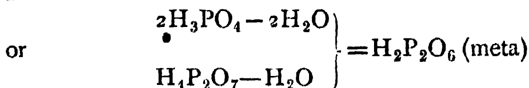
The oxides and acids of phosphorus are entirely different in properties from those of nitrogen, being far more stable, and under no circumstances can they be made to give up oxygen as nitrous and nitric acids do. Orthophosphoric acid can with difficulty be made to crystallise by evaporating its solution in a vacuum over sulphuric acid. On the

application of heat it loses successive proportions of water, thus:—



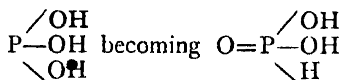
$$2H_3PO_4 - H_2O = H_4P_2O_7 \text{ (pyro)}$$

and



$$\text{or} \quad \left.\begin{array}{l} 2H_3PO_4 - 2H_2O \\ H_4P_2O_7 - H_2O \end{array}\right\} = H_2P_2O_6 \text{ (meta)}$$

Though the dehydration cannot be carried so far as to produce the pure phosphoric oxide, metaphosphoric acid loses water at a red heat, and the residue contains an appreciable excess of the anhydride, P_4O_{10}. It is somewhat remarkable that, although the oxides of phosphorus preserve the complex type of the element, the chlorides are quite simple. The trichloride PCl_3 is a colourless volatile liquid the vapour density of which agrees with the formula. It combines in a direct manner with chlorine, with oxygen, and with sulphur, yielding the pentachloride PCl_5, the oxychloride PCl_3O, and the thiochloride PCl_3S, in all of which the phosphorus appears to be saturated. In contact with water phosphorus trichloride yields phosphorous acid, which would appear from this mode of formation to contain three hydroxyl groups, 3HO. Phosphorous acid is, however, not tribasic but only dibasic, and it is probable, therefore, that internal or isomeric change occurs at the moment of its formation.



$$P\begin{cases} OH \\ OH \\ OH \end{cases} \text{ becoming } O{=}P\begin{cases} OH \\ OH \\ H \end{cases}$$

Phosphoric chloride is a pentachloride, but on vaporisation it dissociates into the trichloride and free chlorine. Evidence of this change is afforded by the colour of the vapour, which is that of chlorine gas, and by the low value observed for the vapour density. This substance is much used as a reagent for exchanging chlorine for hydroxyl.

When dissolved in water it yields hydrogen chloride and orthophosphoric acid. The oxychloride PCl_3O is a colourless volatile liquid which gives a normal vapour density.

Phosphorus forms two compounds with fluorine, namely a trifluoride PF_3, and a pentafluoride PF_5, of which the latter is interesting as it is perfectly stable at high temperatures. Both fluorides are gaseous at common atmospheric temperatures, but are liquefiable under moderate pressure, and the resulting liquids do not attack dry glass.

Phosphorus forms many other compounds with halogens and with sulphur of which no analogues are produced by nitrogen. One compound only of nitrogen with sulphur is known in the form of an orange-coloured crystalline compound having the formula N_2S_2.

CHAPTER XI.

Class II.—Metalloids.

The name *metalloid* obviously belongs to bodies which have the form or appearance of a metal, or which in some way resemble a metal. Hence the impropriety of applying this term, as was formerly done, to such elements as the halogens, to nitrogen, or phosphorus. The name is intended in this volume to designate a body which, although resembling a metal in most characteristics, yet lacks some one or more of the features which true metals generally present. It applies to a somewhat miscellaneous set of bodies. The question of the propriety of including hydrogen amongst them will be discussed presently, but, leaving this one element out of consideration, the test by which the sub-metallic character of most of them may be detected is

the formation of more or less definite oxy-salts. Their oxides are for the most part well-marked anhydric acids, but each of them is capable of producing at least one oxide which possesses basic tendencies more or less pronounced. Still putting hydrogen aside, the metalloids are comparatively imperfect conductors of heat and electricity, and generally brittle. Tin is, however, both malleable and moderately ductile.

METALLOIDS.—I. HYDROGEN.

Hydrogen is the lightest of known gases, its relative density being only ·0693 when the density of air is taken as 1. In this character it is approached only by the inactive element helium, the density of which is about twice as great, but among ordinary chemically active elements nitrogen stands next with a density fourteen times as great. The difficulty of liquefying hydrogen and its very slight degree of solubility in water (coefficient = ·0193) are apparently connected with its low density and small atomic and molecular weights. In the liquid state hydrogen is a clear and colourless liquid which shows no absorption spectrum. It is remarkable for its extraordinarily low density, the specific gravity being represented by the number 0·07 or about $\frac{1}{14}$ of the specific gravity of liquid water. The boiling point of hydrogen is $-252^\circ\cdot5$ or about 21° absolute as determined by a platinum resistance thermometer. This temperature is therefore subject to some future correction. It is interesting to notice that the anticipation that the element in the liquid state would exhibit some of the properties of a metal has not been fulfilled. It more nearly resembles a light paraffin, and may in one sense be considered as the lower homologue of marsh gas or methane.[1] Liquid methane was, previously to the liquefaction of hydrogen, the lightest

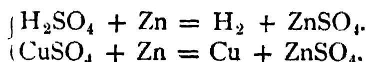
[1] See Homologous series, Chapter XVI.

known liquid, its density at the boiling point being 0·417. From the chemical point of view hydrogen differs from the non-metals in its incapacity to form compounds with all the metals, and in the characters of the few metallic hydrides which are known. Of these the most notable is cuprous hydride Cu_2H_2, a brown solid which is decomposed into its constituents by heat. Other compounds, to which the formulæ Na_4H_2 and K_4H_2 are attributed, are formed by sodium and potassium respectively, and some other similar compounds are believed to exist, but in all cases the hydrides of the metals are solid bodies which are not vaporisable, and which are usually decomposed by heat. On the other hand, hydrogen is, of all the elements, most ready to lend itself to that peculiar state of mechanical combination with metals known as 'occlusion' (p. 21). Palladium, for example, absorbs hydrogen largely, and the charged metal is indistinguishable in appearance from pure palladium, though its conducting power is slightly diminished. This body was regarded by Graham, who discovered it, as the realisation of the long-cherished idea of the essentially metallic character of hydrogen. The solubility of hydrogen in molten metals is also a fact of some interest. Iron, nickel, cobalt, copper, and others when melted in an atmosphere of the gas take up considerable quantities without suffering any alteration in appearance. The gas, however, escapes with effervescence when the metal is allowed to solidify. The title of hydrogen to recognition as a metalloid is based more securely, first, upon the fact that in the electrolysis of water and other compounds it passes along with the metals to the cathode, and is therefore to be ranked with the electro-positive elements; and secondly, upon the resemblance which acids or hydrogen salts bear to metallic salts. In spite of a considerable number of gaseous and liquid exceptions, the majority of known acids are crystallisable bodies, often combining with water of crystallisation, and utterly indistinguishable to all

appearance from ordinary saline compounds. Among common acids, for example, the following are crystallisable :—

Sulphuric acid .	H_2SO_4 (below $-35°$).
Glacial sulphuric acid	H_4SO_5 (below $9°$).
Phosphoric acid .	H_3PO_4.
Boracic acid .	H_3BO_3.
Oxalic acid . .	$H_2C_2O_4 + 2H_2O$.
Formic acid . .	$HCHO_2$ (below $1°$).
Acetic acid . .	$HC_2H_3O_2$ (below $17°$).
Tartaric acid .	$H_2C_4H_4O_6$.
Citric acid . .	$H_3C_6H_5O_7 + H_2O$.
Gallic acid . .	$HC_7H_5O_5 + H_2O$.

But the resemblance between hydrogen salts and metallic salts is not limited to external form. They agree in chemical reactions. When an acid is acted upon by a metal, and hydrogen is expelled, the metathesis is entirely comparable with the exchange of a more positive for a less positive metal of the ordinary recognised class. For example, zinc decomposes hydrogen sulphate, just as it decomposes copper sulphate ; in each case the less positive element is displaced, and a new salt formed.



$$\begin{cases} H_2SO_4 + Zn = H_2 + ZnSO_4. \\ CuSO_4 + Zn = Cu + ZnSO_4. \end{cases}$$

Again, water—that is, hydrogen oxide or hydroxide, H_2O or $H(HO)$— not unfrequently imitates metallic oxides or hydroxides in their chemical reactions. In order to produce exactly the same effect in any given case, it is only necessary to use the water in larger quantity or at a higher temperature.

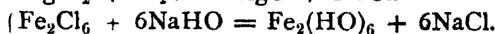
The following are examples of this mode of action :—



$$MgCl_2 + HgO = MgO + HgCl_2.$$



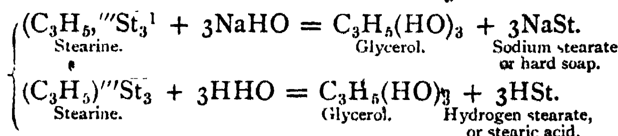
$$MgCl_2 + H_2O = MgO + 2HCl.$$



$$Fe_2Cl_6 + 6NaHO = Fe_2(HO)_6 + 6NaCl.$$



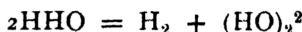
$$Fe_2Cl_6 + 6HHO = Fe_2(HO)_6 + 6HCl.$$



$$\underset{\text{Stearine.}}{(C_3H_5)'''St_3}{}^{1} + 3NaHO = \underset{\text{Glycerol.}}{C_3H_5(HO)_3} + \underset{\text{Sodium stearate or hard soap.}}{3NaSt.}$$

$$\underset{\text{Stearine.}}{(C_3H_5)'''St_3} + 3HHO = \underset{\text{Glycerol.}}{C_3H_5(HO)_3} + \underset{\text{Hydrogen stearate, or stearic acid.}}{3HSt.}$$

Water and acids also undergo electrolysis in the same manner as metallic salts ; *e.g.*



$$2HHO = H_2 + (HO)_2{}^{2}$$

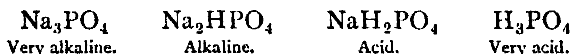


$$2HCl = H_2 + Cl_2$$



$$CuCl_2 = Cu + Cl_2$$

Lastly, it might be pointed out that the sour taste of hydrogen salts and their reddening effect upon vegetable blues are no more to be regarded as indications of peculiar constitution than is the alkaline reaction of many normal metallic salts or the neutrality of others. In such a series as the following we see a gradual transition from strongly alkaline to strongly acid properties :



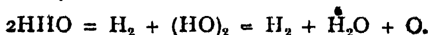
Na_3PO_4	Na_2HPO_4	NaH_2PO_4	H_3PO_4
Very alkaline.	Alkaline.	Acid.	Very acid.

METALLOIDS.—2. TELLURIUM.

Tellurium in many respects closely imitates sulphur and selenion. Thus it forms a gaseous telluretted hydrogen,

[1] $St = C_{18}H_{35}O_2$.

[2] It is a question whether *pure* water is an electrolyte at all, but supposing it to be capable of electrolysis this is probably the first phase in the decomposition, the oxygen which is evolved being due to a secondary reaction, thus :



$$2HHO = H_2 + (HO)_2 = H_2 + H_2O + O.$$

H_2Te, the representative of hydrogen sulphide; also oxides TeO_2 and TeO_3, and acids H_2TeO_3 and H_2TeO_4, corresponding respectively with sulphur dioxide and trioxide, and with sulphurous and sulphuric acids. But tellurium is decidedly metallic in appearance, and forms unstable oxysalts, including a sulphate and nitrate of somewhat uncertain composition.

The following tabular statement will assist the student in comparing together the several members of the group, and will help to indicate the nature of the change which is gradually developed along with increase in atomic weight :

Sulphur S=32·06	Selenion Se=79·1	Tellurium Te=127
Several allotropes; density not exceeding 2·07; m.p. below 120°	Several allotropes; density not exceeding 4·5; m.p. of cryst. variety 217°	Amorphous (?) and crystalline varieties; density of cryst. 6·25; m.p. 455°
H_2S gas	H_2Se gas	H_2Te gas
SO_2 gas	SeO_2 cryst., volatile, soluble	TeO_2 cryst. melts at red heat, almost insol. in water
SO_3 cryst.	SeO_3 unknown	TeO_3 yellow cryst., insol. in water
H_2SO_3 Hydrate cryst.	H_2SeO_3 cryst., sol. in water	H_2TeO_3 amorphous, slightly sol. solid
H_2SO_4 Dense liquid	H_2SeO_4 Dense liquid	H_2TeO_4 cryst. from sol. with $2H_2O$

METALLOIDS.—3. GERMANIUM, TIN, TITANIUM, ZIRCONIUM.

Save for the distinctly metallic character of elemental tin and germanium, and production by tin, germanium, and titanium of an inferior diadic class of derivatives, these elements bear a strong family resemblance to silicon. That the

metallic function is more or less distinctly developed in them, whilst it is altogether imperceptible in silicon, is also indicated by the existence of various oxy-salts, sulphates, phosphates, &c., of tin, titanium, and zirconium, and probably of germanium, similar compounds of silicon being entirely unknown.

The most characteristic compounds of these elements are the chlorides, oxides, and acids in which they play the part of tetrads. The following table affords a synopsis of the chief features of the group:

Silicon $Si = 28{\cdot}4$	Germanium $Ge = 72$	Tin $Sn = 118{\cdot}5$	Titanium $Ti = 48{\cdot}1$	Zirconium $Zr = 90{\cdot}6$
a. amorphous *b.* crystalline melts about 1,200°	cryst., regular octahedrons m.p. 900°	cryst., also malleable; S.G. 7·3 m.p. 232°	cryst., S.G. 4·87 m.p. high	cryst., S.G. 4·15 m.p. high
—	GeO ?	SnO Black powder	TiO ? Black powder	ZrO ? Black powder
SiO_2	GeO_2 cryst. powder slightly sol.	SnO_2 cryst. dimorphous *a.* tinstone corr. to rutile *b.* isomorph. w. brookite	TiO_2 cryst. dimorphous *a.* anatase and rutile dimetric *b.* brookite trimetric	ZrO_2 cryst. artificial isomorph. w. tinstone and rutile
All these dioxides unite with alkaline oxides.				
—	—	—	Tio_3? yellow solid	ZrO_3 white pp.
$SiCl_4$ liquid, b.p. 50°	$GeCl_4$ liquid, b.p. 87°	$SnCl_4$ liquid, b.p. 114°	$TiCl_4$ liquid, b.p. 135°	$ZrCl_4$ solid volatile
SiF_4 liquefiable gas	GeF_4 volatile solid ?	SnF_4 volatile solid ?	TiF_4 fuming liquid	ZrF_4 solid
M'_2SiF_6 Fluosilicates	M'_2GeF_6 Fluo-germanates	M'_2SnF_6 Fluostannates	M'_2TiF_6 Fluotitanates	M'_2ZrF_6 Fluozirconates
Corresponding salts isomorphous.				
SiO_2	GeO_2	SnO_2	TiO_2	ZrO_2
			Isomorphous	
		in tinstone.	in rutile	artificial.

Stannic chloride, stannic methide $Sn(CH_3)_4$ (b.p. 78°) and stannic ethide $Sn(C_2H_5)_4$ (b.p. 181°) are volatile liquids which have normal vapour densities and afford conclusive evidence of the tetrad character of the metalloid in such compounds. But as already mentioned, tin forms an oxide $Sn_{„}O_{„}$, a chloride $Sn_{„}Cl_{2„}$, a sulphide $Sn_{„}S_{„}$ and some other compounds in which it appears to be diad. The chloride is a solid which melts at about 250°, boils at 606° and gives a vapour which, at temperatures even 100° above the boiling point, is greater than would be calculated from the simple formula $SnCl_2$, but does not approach the value required for the double formula Sn_2Cl_4. Hence it is uncertain whether the latter is the true molecular formula as is sometimes supposed. The corresponding ethide is decomposed by heat.

For stannous chloride, representing it as a dichloride there is no counterpart among the compounds of silicon, nor apparently among the remaining elements of the group, for although titanium forms two lower chlorides, the dichloride is wholly different in character from stannous chloride. The formation of a chloride having such well-defined saline characters as stannous chloride, and the existence of various oxysalts of tin, are doubtless connected with the more distinct metallic character of this element as shown, for example, by its malleability. This is again doubtless connected with the relatively high value of its atomic weight. As will be found later, the group may be divided into two subgroups, to the former of which lead is distantly related.

SUBGROUP A.	SUBGROUP B.
Si 28·4.	
	Ti 48·1.
Ge 72.	
	Zr 90·6.
Sn 118·5.	

METALLOIDS.—4. ARSENIC, ANTIMONY, BISMUTH.

(For numerical relations of atomic weights see *Non-metals, Group* 5, p. 175).

These elements are all quinquivalent in their most advanced states of combination, the tendency to assume this condition being the least prominent in the case of bismuth, which is of the whole class the most decidedly metallic.

The analogies of arsenic, antimony, and bismuth will be most satisfactorily brought out by tabulating the formulæ of their leading compounds. For the sake of comparison the corresponding compounds of phosphorus are placed side by side with them.

The vapour densities of phosphorus and arsenic lead to the molecular formulæ P_4 and As_4 for those elements; but antimony and bismuth, though easily fusible metals, are not volatile enough to give vapour at any manageable temperature. Their molecular formulæ are therefore unknown.

It is worthy of note that, as in the case of phosphorus, the vapour densities of the lowest oxides of arsenic and antimony reveal the fact that these compounds preserve the tetratomic grouping. Thus the vapour density of arsenious oxide (white arsenic) is 198. Hence its molecular weight is 396, and its formula is As_4O_6. The vapour density of antimonious oxide also corresponds to Sb_4O_6. By analogy it may be presumed that the oxide of bismuth is similarly constituted. As to the higher oxides of arsenic, antimony, and bismuth, they are all resolved by heat into oxygen and a lower oxide, but analogy with the highest oxide of phosphorus, which has been shown to have the molecular formula P_4O_{10}, leads also to the presumption that they should be similarly represented.

It is somewhat singular that while combination with oxygen is not attended by the separation of the four atoms of the elemental molecule, combination with a halogen

gives in each case a compound containing a single atom of phosphorus, arsenic, antimony, or bismuth.

Among the sulphides the compounds of phosphorus alone have been examined with regard to vapour density and the formulæ P_4S_3 and P_4S_6 are deduced directly from the results. In the case of P_4S_{10} the vapour density actually observed corresponds to half this formula, but there are good reasons for believing that this is due to dissociation of the vapour into a mixture of the lower sulphide and sulphur, $P_4S_6 + S_4$, at the temperature of the experiment.

Phosphorus P = 31	Arsenic As = 75	Antimony Sb = 120	Bismuth Bi = 208·5
	Hydrides and Ethylides.		
PH_3	AsH_3	SbH_3	—
$P(C_2H_5)_3$	$As(C_2H_5)_3$	$Sb(C_2H_5)_3$	$Bi(C_2H_5)_3$
	Chlorides.		
PCl_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
PCl_5	—	$SbCl_5$	—
	Oxides.		
P_4O_6	As_4O_6	Sb_4O_6	Bi_4O_6
P_4O_8		Sb_4O_8	Bi_4O_8
P_4O_{10}	As_4O_{10}	Sb_4O_{10}	Bi_4O_{10}
	Acids.		
HPH_2O_2	—	—	—
—	$HAsO_2$?	$HSbO_2$	$HBiO_2$
H_2PHO_3	H_3AsO_3	—	—
$(HPO_3)_2$	$(HAsO_3)n$	$(HSbO_3)n$	$(HBiO_3)n$
H_3PO_4	H_3AsO_4	H_3SbO_4?	
$H_4P_2O_7$	$H_4As_2O_7$	$H_4Sb_2O_7$	
	Sulphides.		
P_4S_3	—	—	—
—	As_4S_4	—	Bi_4S_4
P_4S_6	As_4S_6	Sb_4S_6	Bi_4S_6
P_4S_{10}	As_4S_{10}	Sb_4S_{10}	—

A few peculiarities exhibited by particular compounds occurring in this table demand notice.

1. The faculty of producing well-defined allotropic modifications shown by phosphorus is not exhibited plainly by the other elements except antimony, which when deposited slowly by electrolysis from a solution of the chloride is producible in the form of a peculiar unstable amorphous modification.

2. The basic property of combining with acids exhibited in a limited degree by phosphine is not displayed by the hydrides of arsenic and antimony. Bismuth forms no compound with hydrogen. The ethyl and corresponding methyl compounds are characterised not so much by a power of combining with acids as by a tendency to unite with O, S, Cl_2, I_2 &c., whereby the central element is brought to a state of saturation as in such compounds as the following :—

Triethyl phosphine oxide	$P(C_2H_5)_3O$
Trimethylarsine sulphide	$As(CH_3)_3S$
Trimethylstibine chloride	$Sb(CH_3)_3Cl_2$

They also unite with alkyl halogen compounds such as CH_3I, C_2H_5Br &c., and thus produce compounds analogous to ammonium salts, for examples,

Tetramethylarsonium iodide $As(CH_3)_4I$.

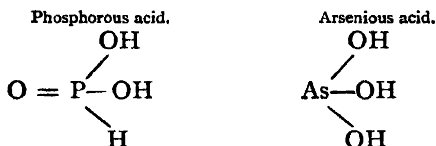
3. No pentachloride, pentabromide, oxychloride or oxybromide of arsenic is known. The pentafluoride is known only in combination with other fluorides.

4. White arsenic occurs in commerce in the form of white masses with conchoidal fracture, often exhibiting a banded appearance, due to the presence of the isomeric vitreous and porcellanous varieties. The former is converted into the latter by pulverisation or by protracted boiling with water. Either variety is but slightly soluble in water, and the solution gives only a feebly acid reaction. Porcellanous arsenic probably owes its opacity to crystalline

structure. By careful sublimation at regulated temperatures white arsenic may be obtained either in the form of transparent regular octahedra or in prismatic crystals of the trimetric system. It is isodimorphous with antimonious oxide.

White arsenic is a feebly basic, as well as acidic, oxide. Its best known salt is the double tartrate $K(AsO)C_4H_4O_6$, which is analogous to the potassio-tartrates of antimony, $K(SbO)C_4H_4O_6$ (tartar emetic), and boron, $K(BO)C_4H_4O_6$.

5. Arsenious acid appears to be normally tribasic, the yellow silver salt containing Ag_3AsO_3. It therefore differs from phosphorous acid, which is dibasic.



6. The orthophosphates and orthoarsenates correspond in every respect with each other, and in many cases with the orthovanadates. In addition to the ordinary salts of the common phosphate type, $M'H_2PO_4$, M'_2HPO_4, and M'_3PO_4, there is a remarkable series of compounds occurring as minerals in combination with a chloride or fluoride.

Apatite	$3[Ca_3(PO_4)_2] \cdot CaF_2$	or $Ca_5(PO_4)_3F$
	or $3[Ca_3(PO_4)_2] \cdot CaCl_2$	or $Ca_5(PO_4)_3Cl$
Pyromorphite	$3[Pb_3(PO_4)_2] \cdot PbCl_2$	or $Pb_5(PO_4)_3Cl$
Mimetine	$3[Pb_3(AsO_4)_2] \cdot PbCl_2$	or $Pb_5(AsO_4)_3Cl$
Vanadite	$3[Pb_3(VO_4)_2] \cdot PbCl_2$	or $Pb_5(VO_4)_3Cl$.

Orthoantimonates and orthobismuthates are unknown, unless we consider the intermediate tetroxides in that light: antimonious orthoantimonate, Sb_2O_4 or $Sb'''(Sb^vO_4)$, and bismuthous orthobismuthate, Bi_2O_4 or $Bi'''(Bi^vO_4)$. Several orthothioantimonates are, however, known; the sodium salt, for example, $Na_3SbS_4.9H_2O$, crystallising readily.

7. The sulphides of arsenic, antimony, and bismuth act as sulphur anhydrides, and in combination with the sulphides of silver, lead, copper, and other metals constitute several interesting minerals.

METALLOIDS.—5. VANADIUM, NIOBIUM, TANTALUM.

This group is connected with the preceding group in virtue of the isomorphism of certain orthovanadates M'_3VO_4 with the corresponding orthophosphates. The vanadates as a rule are, however, more complex than the phosphates, and those which contain the vanadic oxide in excess are usually coloured yellow, orange, or red. Metavanadates $M'VO_3$ and pyrovanadates $M'_4V_2O_7$ also exist, which correspond with meta- and pyro-phosphates respectively, beside a certain number of anhydro-salts, such as sodium tetravanadate $Na_2V_4O_{11} = (NaVO_3)_2.V_2O_5$ and hexvanadate $Na_2V_6O_{16} = (NaVO_3)_2\ 2V_2O_5$, &c.

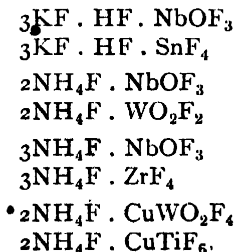
Vanadium in the elemental form is a grey crystalline powder, of specific gravity 5·5, and melting at a very high temperature. Its chief oxide, V_2O_5, is a red crystalline, fusible but non-volatile substance, slightly soluble in boiling water. It forms a few somewhat indefinite oxysalts, but usually acts as an acidic oxide. Orthovanadic acid, H_3VO_4, is not known, but metavanadic acid, HVO_3, is a yellow, crystalline, insoluble powder, sometimes used as a pigment. Pyrovanadic acid, $H_4V_2O_7$, is an unstable brown powder. Vanadium is remarkable for the extensive series of oxides, chlorides, and oxychlorides to which it gives rise, the different stages of oxidation of its dissolved compounds being characterised by a variety of colours, a yellow or red tint belonging to the higher and a blue or green tint especially to the lower oxides, which thus resemble the compounds of chromium, molybdenum, and tungsten. Oxides of phosphorus, arsenic, antimony, and bismuth, except Bi_4O_{10}, are white.

The known oxides of vanadium have the empirical

formulæ V_2O, V_2O_2, V_2O_3, V_2O_4 and V_2O_5 thus running parallel with the series of nitrogen oxides, which, however, as regards physical properties, they in no respect resemble. There are three chlorides; VCl_2 or V_2Cl_4 forming green crystalline scales, VCl_3 forming violet scales, which are deliquescent and soluble in water, and VCl_4 a dark brown liquid which boils and is partially decomposed at 154°. The vapour density appears to correspond to the formula. Vanadium therefore does not maintain the usual persistence of odd or even valency throughout its combinations.

Niobium and tantalum are pentad elements, and are characterised by the production of pentachlorides in the form of yellow crystalline fusible, volatile bodies, the vapour densities of which accord with the formulæ $NbCl_5$ and $TaCl_5$ respectively.

The metals themselves are only known in the condition of black powders, which resist the attacks of most acids, except hydrofluoric acid, in which they are slowly soluble with evolution of hydrogen. Their fluorides unite with the fluorides of the alkali-metals, forming soluble and crystallisable double salts, $2KF,NbF_5$ and $2KF,TaF_5$. But niobium, at least, is also specially characterised by the production of oxyfluorides, which, in combination with the fluorides of the more positive metals, form salts which are isomorphous with the fluotitanates, fluostannates, fluotungstates, and fluozirconates. The following pairs of compounds, for example, crystallise in the same form:—



$3KF . HF . NbOF_3$
$3KF . HF . SnF_4$

$2NH_4F . NbOF_3$
$2NH_4F . WO_2F_2$

$3NH_4F . NbOF_3$
$3NH_4F . ZrF_4$

$2NH_4F . CuWO_2F_4$
$2NH_4F . CuTiF_6$.

It thus appears that groups of elements of different valencies may occasionally replace one another isomorphously, provided the valency of each group as a whole is the same. The radicles which are chemically and isomorphously equivalent to one another in the foregoing compounds are as follows:—

$(NbOF)''$, $(SnF_2)''$, $(WO_2)''$, $(ZrF_2)''$, and $(TiF_2)''$.

Such relations are of precisely the same character as are those of the group $(NH_4)'$, ammonium, to the single metallic atom K'.

The following synopsis will enable the student to perceive the relations of the three elements of this group to one another, and to trace a parallel between them and chromium, molybdenum, and tungsten. This is suggested by a comparison of their atomic weights.

V = 51·2	Cr = 52·1
Nb = 94	Mo = 96
Ta = 183	W = 184.

Vanadium.	Niobium.	Tantalum.
Grey cryst. powder S.G. 5·5	Steel-like metal S.G. 7·06	Black powder element imperfectly known
	CHLORIDES	
—	$NbCl_5$ volatile	$TaCl_5$ volatile
VCl_4 volatile		
VCl_3	$NbCl_3$ grey non-vol.	—
VCl_2		
	OXIDES	
V_2O_5 red fusible indefinite oxysalts	Nb_2O_5 white powder no definite salts	Ta_2O_5 white infusible no definite salts
V_2O_4	Nb_2O_4 Black powder	Ta_2O_4 brown powder
V_2O_3		
V_2O_2	Nb_2O_2	—
VANADATES ortho-, meta-, pyro- and others more complex $M''_3(VO_4)_2$ isomorph. with $M''_3(PO_4)_2$	NIOBATES corresp. wtth meta- and pyrophosphates; usually more complex	TANTALATES corresp. with meta-phosphates; usually more complex

METALLOIDS.—6. MOLYBDENUM, TUNGSTEN, URANIUM.

These elements are heavy metallic substances which since they have been obtained in a pure state and in larger quantity by the use of the electric furnace are known to be malleable and to be hardened by combination with a small quantity of carbon, the products resembling steel.

They appear to be hexads, though, of the three, tungsten alone produces a hexchloride, and that unstable. In the formation of trioxides and volatile dioxydichlorides (general formula $M^{vi}O_2Cl_2$) they resemble chromium, but they differ from that metal in furnishing neither sesquioxide nor monoxide analogous to Cr_2O_3 and CrO.

The series of chlorides is in each case remarkable as illustrating the fact that change of valency does not always occur by pairs of units. This is shown especially in the case of tungsten, which produces a volatile pentachloride WCl_5, beside the hexchloride WCl_6.

The trioxides, MoO_3, WO_3, and UO_3, are generally acidic. Some of the tungstates of the form M'_2WO_4 seem to be isomorphous with the corresponding chromates and sulphates, but the majority are extremely complex, and molybdic and tungstic acids are capable of associating with phosphoric, arsenic, antimonic, and silicic oxides forming compound acids, the salts of which present most remarkable complexity, and the constitution of which is at present a mystery.

These trioxides also exhibit a feebly basic function, the oxy-salts of uranium being the most stable. The nitrate, for example, a yellow crystallisable salt, has the formula $(UO_2)''(NO_3)_2.6H_2O$, and the sulphate and oxalate are formed upon the same type.

Molybdenum and tungsten agree in forming trisulphides, MoS_3 and WS_3, which are unrepresented among the compounds of uranium and of chromium.

The following synopsis includes only the most distinc-

tive of the compounds of the three elements under consideration :—

Molybdenum Mo=96.	Tungsten W=184.	Uranium U=239·5.
Sp. Grav. 9	Sp. Grav. about 19	Sp. Grav. about 19
MoO_3 white fusible volatile	WO_3 yellow fusible vol. at high temp.	UO_3 yellow powder non-volatile
Mo_2O_3 as a hydrate		$U_3O_8 = UO_2 2UO_3$ dark green powder
MoO_2 Brown powder or crystals	WO_2 Brown powder	UO_2 Brown powder
H_2MoO_4 cryst. powder almost insol.	H_2WO_4 yellow almost insol.	H_2UO_4 yellow almost insol.
$MoCl_2$ or Mo_2Cl_4	WCl_2 or W_2Cl_4	
$MoCl_3$ or Mo_2Cl_6		UCl_3 or U_2Cl_6
$MoCl_4$	WCl_4	UCl_4
$MoCl_5$ m.p. 194° b.p. 268°	WCl_5 m.p. 248° b.p. 276°	UCl_5 decomposed by heat
	WCl_6 m.p 275° b.p. 347°	
MoO_2Cl_2	WO_2Cl_2	UO_2Cl_2 known only in combination with chlorides
$MoOCl_4$	$WOCl_4$	

CHAPTER XII.

Class III.—Metals.

Metals are all solids at the temperature of the air, with the sole exception of mercury, which is ordinarily liquid, but solidifies at −40°. The solid metals differ very much in their fusibility, the metals of the alkalies melting most readily (potassium at 62°·5), whilst platinum and its con-

geners require the highest temperature of the oxyhydrogen flame.

Metals, when in a compact state, combine great opacity with high reflective power, exhibiting the appearance which is sufficiently well known as metallic lustre—a property which, however, is exhibited by many other substances, such as iodine, graphite, galena, and many sulphides. Gold in very thin leaves transmits a greenish light.

That all the common metals are heavy is a fact familiar to every one; but an inspection of a table of densities will lead to the conclusion that there are many which are much lighter than the familiar iron, copper, lead, and silver, while there are several which are even heavier than gold. As a curious fact, the heaviest solid known is a metal, osmium (rel. dens. 22·5), and the lightest known *solid* is also a metal, namely, lithium, whose relative density is only ·578.

But it is of much greater importance to observe that in many cases groups of metals which are associated together by reason of community of chemical properties, have also densities which nearly approximate to one another, as shown in the following examples:—

Alkali Metals.

	Density
Lithium	·578
Sodium	·972
Potassium	·865
Rubidium	1·52
Cæsium	1·88

Alkaline Earth Metals.

	Density
Magnesium	1·74
Calcium	1·58
Strontium	2·5
Barium	?

Iron Family.

	Density
Chromium	6·9
Iron	7·8
Manganese	7·4
Nickel	8·9
Cobalt	8·7

Noble Metals.

	Density
Silver	10·5
Palladium	11·5
Rhodium	12·0
Ruthenium	12·0
Gold	19·2
Platinum	21·5
Iridium	21·6
Osmium	22·5

Possibly other similar associations might be discovered, but for the fact that several metals are scarcely known in a compact form, and in other cases the numbers may be more or less incorrect in consequence of the presence of impurity in the specimens operated upon.

With regard to the molecular weights of metals, there is some conflict of evidence in respect to all except the comparatively small number which are vaporisable (see pages 87, 88). From experiments on the lowering of the vapour pressure and of the freezing point of mercury, produced by dissolving small quantities of various metals in mercury, it was thought that the metal dissolved in the form of monatomic molecules. Other more recent work, however, throws considerable doubt on this conclusion.

The following are the chief characteristics of metals as a class:—

1. Metals are the best conductors of heat. They differ widely among themselves in this respect, as the following

rough comparison shows. Silver, as the best conductor, is placed at the head of the list. The numbers may be taken to represent the relative lengths of bars of equal diameter which, by applying a common source of heat to one extremity, would become equally heated in the same time.

Silver	1000
Copper	736
Gold	532
Iron	119
Lead	85
Platinum	84
Bismuth (an imperfect metal)	18

2. Metals are the best conductors of electricity. The metals given in the foregoing list stand in nearly the same order as regards electric conductivity.

3. Metals are almost always malleable, though in a few cases—zinc, for example—this happens only at slightly elevated temperatures. Frozen mercury is malleable.

4. Many metals are ductile, but, since ductility is so largely dependent upon tenacity, it by no means follows that ductility should be manifested by a given metal in the same degree as malleability. Gold, for example, is by far the most malleable metal, though in point of ductility it is surpassed by platinum. Lead and tin, though easily rolled into sheet, can scarcely be obtained in the form of wire, owing to their very slight tenacity.

5. Metals are all *positive* in their electrochemical relations toward the rest of the elements, and in the electrolysis of their compounds appear, as hydrogen does, at the cathode. The oxides of metals are very generally basic.

The basigenic character belongs exclusively to the metals and metalloids. But the oxygenic or acidic function is discharged almost equally well by particular elements in all three divisions.

The transition from metal to non-metal is, therefore,

not accomplished by any sudden break, and the student must be prepared to encounter great, and perhaps insurmountable, difficulties in any attempt to establish a line of demarcation between them.

The following series of oxides will serve to indicate how gradually the one character disappears as the other is developed. The symbols in black type represent basic oxides, those in roman represent oxides which go to the negative side of the salts into which they enter.

From Non-metallic to Metallic.


SO_3 WO_3 CrO_3 FeO_3


SO_2 WO_2


Cr_2O_3 **Fe_2O_3** **Ni_2O_3**
No Salts.


CrO **FeO** **NiO** **CuO**
Extremely oxidisable.


Cu_2O **Ag_2O**
Salts unstable.

METALS.—I. THE METALS OF THE ALKALIS. MONADS.

Lithium, Li	= 7·03	$\frac{Li+K}{2}=23\cdot09$
Sodium, Na	= 23·05	
Potassium, K	= 39·15	
Potassium, K	= 39·15	$\frac{K+Cs}{2}=86\cdot07$
Rubidium, Rb	= 85·4	
Cæsium, Cs	= 133	

Salt Type, M'Cl.

These are soft, white, light, easily fusible, and somewhat volatile metals. They oxidise rapidly in the air, but differ materially from one another in this respect, their affinity for oxygen increasing with the atomic weight. This is shown especially by the spontaneous inflammability of rubidium, and the impossibility of obtaining cæsium by decomposition of its carbonate with charcoal. They all decompose cold

water with formation of a soluble hydroxide and evolution of hydrogen gas. But as a consequence of the inferior energy of lithium and sodium, the heat developed by their action upon water is not sufficient to cause the ignition of the escaping hydrogen, whereas the hydrogen disengaged by potassium inflames instantly, and continues to burn with a purple light, due to the accompanying vapour of the metal.

The hydroxides of these metals are all fusible, scarcely decomposed by heat, but volatilise at high temperatures; they are very soluble in water, and the solutions are caustic to the skin, alkaline to litmus, and absorb carbonic acid from the air. The hydroxides also saponify oils and fats, and the resulting soaps are alkaline and soluble.

The chlorides, sulphides, sulphates, phosphates, and carbonates of the alkali metals are all soluble in water, and their chlorides and sulphates yield perfectly neutral solutions. The sulphates combine with the sulphate of aluminium and the allied metals, generating highly characteristic double salts, called 'alums,' which crystallise in octahedrons. A crystallised lithium-alum has not yet been described, but this is probably owing to its great solubility.

The alkali salts all communicate intense and characteristic colours to the Bunsen flame, and the spectrum of the light so produced exhibits in each case a comparatively small number of bright lines.

As indicated by the atomic weights, the alkali metals may be divided into two sub-groups. In the one we have potassium, cæsium, and rubidium, which are distinguished by greater chemical activity and inferior solubility of their salts, notably of the platinochlorides and acid tartrates.



K_2PtCl_6	$KHC_4H_4O_6$
Rb_2PtCl_6	$RbHC_4H_4O_6$
Cs_2PtCl_6	$CsHC_4H_4O_6$

Sodium and lithium, though entirely comparable with potassium, are yet distinguished from it by much feebler

chemical energies, by the solubility of their platinochlorides, acid tartrates, and alums, and by different minor peculiarities. Sulphate of sodium, for example, crystallises with ten molecules of water, while sulphate of potassium is anhydrous. The carbonates also differ, that of sodium forming large efflorescent crystals containing $10H_2O$, the carbonate of potassium occurring in small deliquescent granules, containing usually about one or two molecules of water.

Both sodium and potassium yield unstable peroxides, Na_2O_2 and K_2O_2, and potassium is even capable of passing to a higher stage of oxidation, the product being a tetroxide K_2O_4. No salts corresponding with these oxides exist.

METALS.—2. METALS OF THE ALKALINE EARTHS. DIADS.

$$\left.\begin{array}{lll}\text{Calcium,} & Ca = & 40 \\ \text{Strontium,} & Sr = & 87{\cdot}6 \\ \text{Barium,} & Ba = & 137{\cdot}4\end{array}\right\} \frac{Ca + Ba}{2} = 88{\cdot}7$$

Salt Type, $M''Cl_2$.

These three metals, originally obtained in an impure state by the electrolysis of their fused chlorides, were described as having a yellowish colour. Calcium alone appears to have been obtained in a state of purity either by heating anhydrous calcium iodide with sodium, or by electrolysis of the fused salt. Calcium crystallises in white hexagonal crystals, which when heated in hydrogen or nitrogen absorb these gases freely. The hydride CaH_2 is a white crystalline substance.

These metals are less oxidisable than the metals of the alkalies, though they are still capable of decomposing cold water. They also communicate characteristic colours to flame, and yield spectra which are easily recognisable but somewhat more complex than those of the alkalis generally.

The hydrates of the alkaline earths, that is the

hydroxides of calcium, strontium, and barium, are white substances which are decomposed by heat into water and the anhydrous oxides. They are far less soluble in water than the alkalis, and are proportionately less caustic, alkaline, and attractive of carbonic acid. They saponify fats, but the resulting soaps are generally insoluble in water.

The salts of barium, strontium, and calcium are, as a rule, perfectly neutral.

The chlorides and sulphides are soluble in water, but the sulphates, phosphates, and carbonates are insoluble.

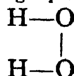
Oxide of barium or baryta exposed to a current of air or oxygen at a heat short of redness absorbs oxygen, and becomes converted into a peroxide, BaO_2. The corresponding peroxides of strontium and calcium are obtained as white precipitates by adding solution of hydrogen peroxide to lime or strontia water. All three are resolved by ignition into oxygen gas and a residue of the protoxide. They are also soluble in hydrochloric acid, yielding peroxide of hydrogen and the chloride of the metal, *e.g.*—



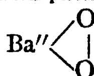
$$BaO_2 + 2HCl = BaCl_2 + O_2H_2.$$

Hence it is presumable that they have the same constitution as hydrogen peroxide, the oxygen atoms partly satisfying each other's attractions, according to the following graphic formulæ :—

Hydrogen peroxide.



Barium peroxide.



Of the three elements, barium, with the highest atomic weight, is decidedly most basylous. Strontium standing next is, in respect to some characters, more nearly related to barium than to the third member of the series, calcium. Thus the nitrates of strontium and barium crystallise in anhydrous octahedrons, isomorphous with lead nitrate, $Pb(NO_3)_2$. The sulphates of these two metals are also anhydrous, and are practically insoluble in water and acids.

Nitrate of calcium is a deliquescent salt, soluble in alcohol and crystallising in prisms, which contain $Ca(NO_3)_2.4H_2O$. Its sulphate, in the form of gypsum, combines with two molecules of water, is perceptibly soluble in water, and much more freely so in hydrochloric acid.

On the other hand, strontium agrees witn calcium in the production of a deliquescent chloride, which is soluble in alcohol, while the barium chloride is insoluble in alcohol.

The crystallised chlorides have the following formulæ:—

Chloride of	Calcium,	$CaCl_2 . 6H_2O$
,,	Strontium,	$SrCl_2 . 6H_2O$
,,	Barium,	$BaCl_2 . 2H_2O$

METALS.—3. ZINC GROUP. DIADS.

$$\left.\begin{array}{lll} \text{Magnesium,} & Mg = & 24\cdot36 \\ \text{Zinc,} & Zn = & 65\cdot4 \\ \text{Cadmium,} & Cd = & 112 \end{array}\right\} \frac{Mg + Cd}{2} = 68\cdot18.$$

Salt Type, $M''Cl_2$.

These elements are rightly associated together in consequence of a very obvious seriation of properties, notwithstanding that they are less intimately related to one another than, for example, the metals of the alkaline-earth family. Magnesium is a white metal, zinc and cadmium faintly bluish white, and all three are volatile. Their volatility somewhat strangely increases in proportion as the atomic weight increases, while their basigenic power diminishes. That zinc is decidedly more positive than cadmium is shown by its power of precipitating cadmium in the metallic state from its solutions. That magnesium is more positive than the other two is shown by its power of decomposing water when heated with it, or more readily if previously coated with pulverulent copper.[1] Also by the precipitation

[1] Zinc and cadmium, when coated with spongy copper, are also capable of decomposing water slowly.

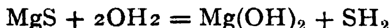
of both zinc and cadmium when metallic magnesium is introduced into solutions of their salts.

Magnesium, zinc, and cadmium are all easily combustible in air or oxygen, the combustion being attended by the emission of a dazzling light. Each metal forms one oxide: MgO, a white unalterable powder; ZnO, a white powder, becoming yellow when heated; CdO, a yellowish brown powder. These oxides are almost insoluble in water, that of magnesium only showing a faint alkaline reaction when placed upon wet test-paper. The oxides and hydroxides are readily soluble in solutions of ammoniacal salts.

The hydroxides are easily resolved, by being heated, into water and the oxide, and the carbonates in like manner give up carbon dioxide, leaving a residue of the oxide.

The chlorides are volatile, deliquescent solids.

The sulphide of magnesium is an earthy substance which is decomposed even by water—



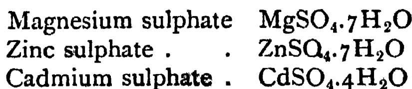
$$MgS + 2OH_2 = Mg(OH)_2 + SH_2$$

and is therefore not precipitated on the addition of a soluble sulphide to a magnesian solution.

Zinc sulphide (native = blende) is a white precipitate easily soluble in diluted mineral acids, and hence only imperfectly precipitated by the action of hydrogen sulphide upon the solution of a zinc salt.

Cadmium sulphide (native = greenockite) is a yellow precipitate thrown down by hydrogen sulphide from acidified solutions of cadmium salts.

The sulphates of these metals are, perhaps, the most characteristic of their salts. They are soluble in water, and have the following formulæ:—

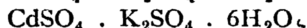


Magnesium sulphate	$MgSO_4.7H_2O$
Zinc sulphate . .	$ZnSO_4.7H_2O$
Cadmium sulphate .	$CdSO_4.4H_2O$

The magnesium and zinc salts crystallise in four-sided prisms, isomorphous with the corresponding nickel sulphate.

All three combine with potassium sulphate, generating double salts, which crystallise with six molecules of water:


$MgSO_4 . K_2SO_4 . 6H_2O$

$ZnSO_4 . K_2SO_4 . 6H_2O$

$CdSO_4 . K_2SO_4 . 6H_2O$.

Sulphates isomorphous with these are produced by several other metals, such as copper and iron, and will be referred to in the proper place.

A general review of its properties indicates that magnesium forms a connecting link between zinc and calcium. From the latter it differs in the insolubility of its hydroxide in water, and in the solubility of the same compound in ammonium chloride. Sulphate of magnesium is also distinguished from sulphate of calcium by its ready solubility in water.

METALS.—4

Mercury Hg = 200·3

Mercury is a white metal which is distinguished from all other metals by its remarkable fusibility and volatility. When solid (m.p.—38°·8) it crystallises in the regular system, and is both ductile and malleable. Mercury is easily reduced to the metallic state, either by heating its oxides and oxysalts, or by electrolysis of solutions of any of its salts or by contact with such metals as zinc, iron or even copper. The vapour density of this metal is the half of its atomic weight, hence like zinc and cadmium its molecule is monatomic and is represented by symbol Hg. It is incapable of decomposing steam or hydrogen chloride but it is slowly oxidised when heated in air or oxygen, and is converted into sulphate by the action of hot concentrated sulphuric acid, sulphur dioxide being evolved.

The compounds of mercury are divisible into two classes, the mercuric and mercurous, corresponding to the

two chlorides $HgCl_2$ and Hg_2Cl_2 or the two oxides HgO and Hg_2O.

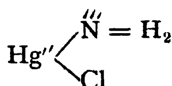
The *mercuric salts* are almost without parallel as regards properties among metallic salts; their formulæ generally correspond with those of the salts of cadmium and zinc, but there are many points of difference noticeable, for example, in the proportion of water of crystallisation.

The following are the most important mercuric compounds:—

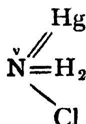
Oxide, HgO. A red or yellow powder darkening by heat, and decomposed below redness into Hg and O_2.

Chloride, $HgCl_2$. White, crystallisable, soluble in water, alcohol, and ether. Vapour density $\frac{200 + 71}{2} = 135 \cdot 5$.

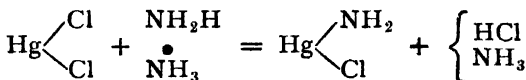
Amidochloride, $HgNH_2Cl$. Commonly known as 'White Precipitate.' Representable either as an amidochloride,



or as chloride of mercuric ammonium,



The former view is perhaps preferable, considering its formation from mercuric chloride by ammonia.

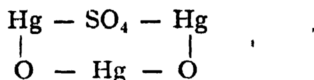


Iodide, HgI_2. Red or yellow, dimorphous, insoluble in water, soluble in ether and in solution of potassium iodide.

Sulphide, HgS. A black precipitate or, in the form of cinnabar, dark red masses of hexagonal prisms. Artificial vermilion, bright red powder.

Sulphate, $HgSO_4$. Colourless, minute, prismatic crystals,

characteristically decomposed by water with formation of yellow 'turpeth mineral,' $Hg_3O_2SO_4$, which may be regarded as trimercuric orthosulphate, $Hg''_3(SO_6)^{vi}$ (see p. 169), or as a basic salt.



The *mercurous salts*, on the other hand, resemble in many respects the corresponding compounds of silver.

Silver oxide, Ag_2O, and mercurous oxide, Hg_2O, are both nearly black, insoluble in water, and resolved by heat into oxygen gas and the metal.

Silver chloride, $(AgCl)_n$, and mercurous chloride, Hg_2Cl_2, are both obtainable by precipitation as white powders, which blacken, the silver salt quickly, the mercury salt slowly, on exposure to light.

Silver iodide $(AgI)_n$ and mercurous iodide Hg_2I_2 are both yellow and insoluble in water and dilute acids.

Silver nitrate $AgNO_3$ is soluble in water without apparent decomposition, and the solution is neutral. Mercurous nitrate $Hg_2(NO_3)_2.4H_2O$ crystallises in monoclinic prisms which, though soluble in a small quantity of water without obvious change, are decomposed by a larger quantity yielding an acid solution with a deposit of basic salt. The chief distinction between silver and mercurous compounds, however, lies in the volatility of the latter.

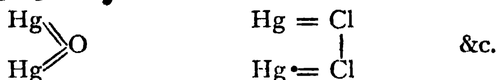
The low vapour density of calomel, 117.75 approximately, has been traced to dissociation into vapours of mercuric chloride and mercury. This compound and consequently all other mercurous compounds may be supposed to contain diad mercury and the formulæ are usually written as follows:—



As, however, mercury in the free state in vapour shows

no signs of association of the atoms it seems improbable that they should thus combine together in the presence of a second element.

Possibly these compounds may be represented as formed of diad mercury united to the second element in virtue of the extra capacity for combination which they are known under certain circumstances to be capable of developing; thus



The following table shows that the properties of mercury are nearly those which might be anticipated from its atomic weight and the assumption that it is related, though distantly, to cadmium.

	At. Wt.	Approximate. Density	M.P.	B.P.	V.D.
Mg	24·36	1·7	800°	?	?
Zn	65·4	7·0	433°	930°	32·5
Cd	112·4	8·6	320°	746°	56
Hg	200·3	(liq.)13·6	— 39°	357°	100

METALS.—5.

Thallium, Tl = 204·1.

Triad. Salt types $M'Cl$, *and* $M'''Cl_3$.

Lead, Pb = 206·9.

Tetrad. Salt types, $M''Cl_2$, *and* $M^{IV}Cl_4$.

Thallium was originally discovered and occurs most abundantly in certain kinds of copper and iron pyrites. It is a very soft, nearly white metal, which tarnishes quickly but superficially in the air. It closely resembles lead in physical properties, except that it is softer and streaks paper more readily. It melts at 294°, and volatilises at a red heat. It is capable of burning brilliantly in oxygen.

Thallium forms two classes of compounds, those in which it is univalent being the more stable.

The following are the most characteristic of *thallous* compounds:—

Chloride, TlCl. A white curdy precipitate, resembling silver chloride, but crystallisable from boiling water, and combining with platinic chloride to form a yellow, slightly soluble, crystalline compound, Tl_2PtCl_6.

Oxide, Tl_2O, and *Hydroxide*, TlHO. These compounds are soluble in water, the solution being strongly alkaline, and reacting in the same manner as caustic potash. The hydroxide differs from the alkali hydroxides in losing the elements of water when exposed over oil of vitriol in a vacuum. The residual oxide is almost black, and after fusion crystalline.

Sulphate, Tl_2SO_4. A soluble colourless salt, isomorphous with sulphate of potassium. It combines with aluminium sulphate, forming a true alum, $TlAl(SO_4)_2.12H_2O$.

Sulphide, Tl_2S. A brown precipitate, soluble in acids.

Thallic Compounds.—Chloride, $TlCl_3$. A soluble salt, crystallisable by evaporation of its solution in a vacuum. It melts and evolves chlorine at high temperatures. It combines with the monochloride, forming two compounds, Tl_4Cl_6 or $3TlCl.TlCl_3$, and Tl_2Cl_4 or $TlCl.TlCl_3$. It forms similar compounds with the chlorides of potassium and ammonium.

Oxide, Tl_2O_3. A dark red powder, insoluble in water, and reduced by heat to thallous oxide. Thallium is readily obtained from its salts either by electrolysis, by the action of zinc, or by fusion with cyanide of potassium.

The ordinary spectrum of thallium is the simplest known. It consists of a single bright line in the green.

LEAD is a bluish metal, so soft as to streak paper, and possessing very little tenacity. Its specific gravity is 11·36, a number very near to, and intermediate between, that of thallium, 11·9, and of silver, 10·53. The latter metal is

very constantly associated with it, occurring as sulphide in, probably all, galena. Lead melts at 326°, and at a red heat volatilises freely. A freshly cut surface tarnishes rapidly in air, but oxidation, except of the melted metal, does not proceed to any appreciable extent.

Lead forms two oxides of definite composition, namely, litharge, PbO, and the peroxide, PbO_2, besides several mixed oxides containing the elements of these two in various proportions. The red oxide is generally $2PbO, PbO_2$, or Pb_3O_4. When plumbic peroxide is acted upon by hydrochloric acid, it does not, like barium peroxide, give rise to hydrogen peroxide, but to a tetrachloride, $PbCl_4$. In these two compounds, therefore, lead is quadrivalent, and their formulæ must be written as follows:—



The tetrachloride is a very unstable compound, but a crystallised tetracetate $Pb(C_2H_3O_2)_4$ and tetrapropionate $Pb(C_3H_5O_2)_4$ are easily obtained by dissolving red lead in the corresponding acids. Several double fluorides and chlorides are also known in which the lead is quadrivalent. These are appropriately called *plumbic* salts, while the name *plumbous* should be applied to the ordinary salts. The latter are represented by the following compounds:—

The *dichloride*, $PbCl_2$, a white, sparingly soluble salt, crystallisable from boiling water.

The *oxide*, PbO, is a dull yellow, the hydroxide a white powder. Both are slightly soluble in water, the solubility, like that of lime, being increased by the addition of sugar. The solutions are strongly alkaline, and absorb carbonic acid from the air.

Sulphate, $PbSO_4$. In the form of lead-vitriol, isomorphous with heavy spar, $BaSO_4$.

Carbonate, $PbCO_3$. As white-lead ore or cerusite, isomorphous with witherite, $BaCO_3$.

Nitrate, Pb $(NO_3)_2$, crystallises in octahedrons, isomorphous with barium nitrate.

Sulphide, PbS. Black insoluble powder or crystallised in shining cubes (galena).

Relations of Thallium and Lead.

The relations of thallium both to potassium and lead are exceedingly well marked. With potassium it agrees in the alkalinity of its oxide and the characters of the platinochloride, acid tartrate, sulphate, and alum. But it differs from potassium and resembles lead in the ready reducibility of the metal, in its high atomic weight and density, and in the characters of the sulphide, monochloride, and other salts.

Lead, in its turn, has strong points of resemblance on the one hand to thallium, and on the other to barium, as indicated by the isomorphism of many lead and barium salts.

Lead therefore is related to the alkaline earth metals in the same way that thallium is related to the metals of the alkalis; thus:—

Atomic Weights.			Atomic Weights.
206·9	Pb″	Tl′	204·1
137·4	Ba	Cs	133·
87·6	Sr	Rb	85·4
40·	Ca	K	39·15

METALS.—6. ALUMINIUM GROUP.

Aluminium, Al = 27·1
Gallium, Ga = 70·
Indium, In = 114·

Triads or quasi-tetrads. Salt type, MCl_3.

These are white metals of comparatively low density, standing towards one another in a position which is the counterpart of that shown by the group magnesium, zinc, cadmium.

Aluminium is a very abundant constituent of various silicates. It forms a single oxide and a series of salts which are closely related to the corresponding compounds of iron, as will be shown in the next group.

Gallium and indium, on the other hand, are very rare elements occurring in certain zinc ores. They differ from aluminium in their lower fusing points, and in the formation of more stable sulphides. The following tabular statement will recall their chief characteristics.

	Aluminium.	Gallium.	Indium.
Density	2·6	5·9	7·4
Melting point	750°–800°	30°	176°
Chloride	$AlCl_3$ (at 760° and upwards)	$GaCl_3$	$InCl_3$
Oxide	Al_2O_3 white	Ga_2O_3 white	In_2O_3 yellow
Alum $\left.\begin{matrix} M' \\ M''' \end{matrix}\right\} (SO_4)_2 12H_2O$	Octahedral	Octahedral	Octahedral
Sulphide	Decomposed by water	Precip. only in company with ZnS	Yellow precipitate

METALS.—7. IRON GROUP.

Chromium, Cr = 52·7.

Hexad. *Salt types,* $M''Cl_2$ *and* $(M_2)^{VI}Cl_6$.

$\left.\begin{matrix} \text{Manganese, Mn} = 55 \\ \text{Iron, Fe} = 56 \end{matrix}\right\}$

Hexad. *Salt types* $M''Cl_2$ *and* $(M_2)^{VI}Cl_6$.

$\left.\begin{matrix} \text{Cobalt, Co} = 59 \\ \text{Nickel, Ni} = 58{\cdot}7 \end{matrix}\right\}$

Tetrad. *Salt type,* $M''Cl_2$.

These are white or grey metals of very high melting point. Their relative densities follow one another in the same order as the atomic weights, and are almost directly proportional to them. They may be placed in the following order, which we shall show presently represents very fairly their mutual chemical relations :

Atomic Weight.		Relative Density.
52·1	Cr	6·8 to 7·3

Atc. Wt.		Rel. Dens.	Atc. Wt.		Rel. Dens.
55	Mn	8·0 (about)	56	Fe	7·8
59	Co	8·9	58·7	Ni	8·6

Al	Cr	Fe
No Aluminous Compounds known.	$CrCl_2$ $CrSO_4 7H_2O$? pale blue	FeO $FeCl_2$ $FeSO_4 . 7H_2O$ pale green
	$\left.\begin{matrix} CrSO_4 \\ K_2SO_4 \end{matrix}\right\} 6H_2O$	$\left.\begin{matrix} FeSO_4 \\ K_2SO_4 \end{matrix}\right\} 6H_2O$
		isomorphous with
All Aluminic Compounds Colourless.	Cr_3O_4	Fe_3O_4
Al_2O_3	Cr_2O_3	Fe_2O_3
$AlCl_3$ volatile.	Cr_2Cl_6 or $CrCl_3$ violet : volatile at red heat.	Fe_2Cl_6 or $FeCl_3$ green : volatile at red heat
$Al_2(SO_4)_3$	$Cr_2(SO_4)_3$	$Fe_2(SO_4)_3$
$AlK(SO_4)_2 . 12H_2O$	$CrK(SO_4)_2 \cdot 12H_2O$	$FeK(SO_4)_2 . 12H_2O$
		modified —(FeS_2)
	CrO_2Cl_2	—
	CrO_3	—
	CrO_4K_2	FeO_4K_2
	CrO_4Ba	FeO_4Ba
	$\left\{\begin{matrix} CrO_4K_2 \\ CrO_3 \end{matrix}\right.$ or $\left\{\begin{matrix} CrO_2 . OK \\ O \\ CrO_2 . OK \end{matrix}\right.$	—
	$\left\{\begin{matrix} CrO_4K_2 \\ 2CrO_3 \end{matrix}\right.$ or $\left\{\begin{matrix} CrO_2OK \\ O \\ CrO_2 \\ O \\ CrO_2OK \end{matrix}\right.$	—
	$Cr_2O_6(OH)_6$?	—

Ni	Mn	Co
NiO $NiCl_2$ $NiSO_4.7H_2O$ bright green	MnO $MnCl_2$ $MnSO_4.7H_2O$ pale pink	CoO $CoCl_2$ $CoSO_4.7H_2O$ bright red
$\left.\begin{matrix}NiSO_4\\K_2SO_4\end{matrix}\right\}6H_2O$	$\left.\begin{matrix}MnSO_4\\K_2SO_4\end{matrix}\right\}6H_2O$	$\left.\begin{matrix}CoSO_4\\K_2SO_4\end{matrix}\right\}6H_2O$
corresponding magnesium salts.		
—	Mn_3O_4	Co_3O_4
Ni_2O_3	Mn_2O_3	Co_2O_3
No Salts	Mn_2Cl_6 or $MnCl_3$ decomposed by heat	Co_2Cl_6 or $CoCl_3$ decomposed by heat
—	$Mn_2(SO_4)_3$?	$Co_2(SO_4)_3$?
—	$MnK(SO_4)_2 12H_2O$	—
cubes or regular octahedrons.		
—(NiS_2)	MnO_2	—
—	MnO_2Cl_2	—
—	MnO_3	—
—	MnO_4K_2	—
—	MnO_4Ba	—
—	—	—
—	—	—
—	—	—
—	—	—
—	MnO_3OH and Mn[illegible]O	—

These metals resist atmospheric oxidation to a considerable extent, except moisture or carbonic acid be present. Several of them, especially iron and manganese, are capable of decomposing steam at a red heat with evolution of hydrogen. They all dissolve more or less rapidly in dilute acids. Iron, cobalt, and nickel are strongly paramagnetic, chromium and manganese feebly so.

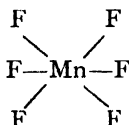
A synoptical view of the chemical relations of these metals to one another will be best obtained, since they are somewhat complex, by tabulating the formulæ of their most characteristic compounds as on the preceding page. The chief compounds of aluminium have been added by way of comparison and for the sake of recalling the isomorphism of alumina and ferric oxide. Few observations upon the table are necessary. As in all similar groups of intimately related elements, each one seems to affect a particular state of oxidation or combination in which it attains a condition of chemical repose or equilibrium. Thus the aluminic salts are absolutely irreducible to any lower state of oxidation; chromic salts reducible with great difficulty; ferric salts are easily transformed into ferrous, whilst manganic salts evolve chlorine or oxygen by mere ebullition. The isomorphous relations of these metals to one another are of great interest, and are exhibited not only by the alums and other artificial salts, but in the constant association of these metals in nature, as, for example, in the replacement of aluminium by iron in clays, and in the silicates from which they are formed, in the replacement of the elements of ferric oxide by chromic oxide in chrome-iron, $FeO.Cr_2O_3$, and by the occurrence of metallic nickel in meteoric iron.

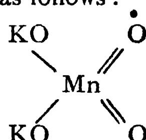
Several members of the group exhibit peculiarities which are well worthy of study, but in this place can receive only passing notice. Such, for example, are the metameric (?) modifications of alumina and of chromic salts, indicated in the latter case by curious changes of colour and solubility; also the remarkable influence of a small quantity of carbon

in increasing the fusibility and hardness of all the metals of the group; also the production of an extensive series of ammoniacal bases by cobalt, not by nickel.

Valency of the Iron Group.

Manganese forms a sexfluoride, MnF_6, and a class of salts, the manganates, which are said to be isomorphous with the chromates and sulphates. Hence manganese is sexivalent, and the formulæ of manganic perfluoride and potassic manganate may be written as follows:





Manganese also forms a dioxide in which it is quadrivalent,

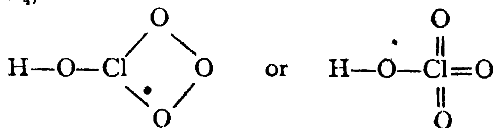


and a chloride corresponding with ferrous chloride in which it may be considered bivalent,



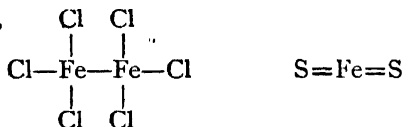
It appears that the molecular formula of potassium permanganate is $KMnO_4$ and not, as formerly written, $K_2Mn_2O_8$. Consequently manganese must be either triad, as it appears to be in the manganic chloride, or it may be heptad.

The isomorphism of the permanganates and perchlorates is explainable on the assumption that both chlorine and manganese are triad or heptad in the formulæ $HClO_4$ and $HMnO_4$, thus

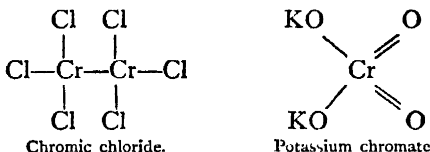


By reason of the correspondence between the ferrates and manganates, iron must also be regarded as hexad; although in ferric, and probably also ferrous compounds, it is often assumed to be tetrad.

Thus the vapour density of ferric chloride at moderate temperatures[1] agrees with the half of the molecular weight denoted by the formula Fe_2Cl_6. The existence of iron pyrites, FeS_2, the analogue of SnS_2, also supports the hypothesis of the quadrivalence of iron in these compounds.



Chromium is also tetrad in its ordinary chromic salts, but hexad in the chromates, as well as in chromium sexfluoride, trioxide, and oxychloride.



Chromic chloride. Potassium chromate

The ordinary salts of cobalt and nickel correspond to the ferrous and zinc salts, but they form unstable peroxides, Co_2O_3 and Ni_2O_3, which lose oxygen at a red heat.

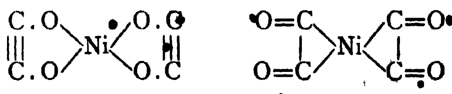
Cobalt forms a still higher oxide which is stated to be a dioxide. It forms green very unstable alkali salts which are soluble in water.

Among the most remarkable compounds formed by metals are the compounds which nickel especially and iron form with carbon monoxide. The formula of the nickel compound, which is confirmed by reference to its vapour

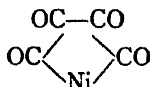
[1] At high temperatures decomposition takes place into ferrous chloride and chlorine.

density, is $Ni(CO)_4$. Iron forms a pentacarbonyl, $Fe(CO)_5$, a viscid liquid, which crystallises at low temperatures. Attempts to produce corresponding compounds with the closely related metals cobalt and manganese have failed.

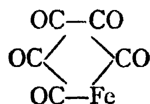
The constitution of these compounds is not understood. The nickel compound may be represented by either of the following formulæ—



Or more probably—



And the iron carbonyl in a similar manner—



Metals.—8.

Copper, Cu = 63·6
Silver Ag = 107·93.

Salt-types, $(M_2)''Cl_2$ and $M''Cl_2$.

Copper is distinguished from the members of the series just considered by its red colour, by its very superior conductivity of heat and electricity, by its diamagnetic properties, and by the easy reduction of the metal from its oxide and salts, also by its indifference to diluted sulphuric or hydrochloric acid. It is further characterised by the fact that no basic oxide superior to the oxide CuO can be isolated, by the production of a suboxide, Cu_2O, and corresponding series of salts, also by the facility with which

many of its compounds unite with ammonia. By the last two characters a relationship to silver and mercury is indicated.

The following are the most important of the compounds of copper, together with the formulæ of compounds with which they manifest greater or less analogy :—

Cuprous.	Mercurous.	Argentic.
Cu_2O	Hg_2O	Ag_2O
or	or	or
Cu	Hg	Ag
| >O	| >O	| >O
Cu	Hg	Ag
Cu—Cl	Hg—Cl	Ag—Cl
|	|	|
Cu—Cl	Hg—Cl	Ag—Cl
Cu—H		
|	No hydride.	No hydride.
Cu—H		

Cu_2S isomorphous with Ag_2S and with CuAgS.

Very few cuprous oxysalts are known, for when cuprous oxide is acted upon by acids it generally splits up and yields a cupric salt and a residue of metallic copper.

Cupric.		Iron and Manganese.
CuO		FeO
$CuSO_4.5H_2O$	isomorphous with	$FeSO_4.5H_2O$
	and with	$MnSO_4.5H_2O$
$\left.\begin{matrix}CuSO_4\\K_2SO_4\end{matrix}\right\}6H_2O$	isomorphous with	$\left.\begin{matrix}FeSO_4\\K_2SO_4\end{matrix}\right\}6H_2O$
CuS		FeS
$FeCuS_2$		
or $Fe_2Cu_2S_4$		FeS_2
Copper pyrites.		Iron pyrites.

Considering the very general blue or green colour of the cupric salts, and their dissolution in excess of ammonia to form a blue liquid, copper approaches more nearly to nickel

than to any other member of the iron group. And although a pentahydrated nickel sulphate corresponding with common blue vitriol has not been described, yet of the isomorphism of copper and nickel in the form of sulphate there can be no doubt. For when a mixture of cupric and nickel sulphates is crystallised, the crystals which are deposited, though containing both nickel and copper, have the form of nickel sulphate, and contain seven molecules of water when the nickel is in excess. If, on the other hand, the cupric sulphate is in excess, the crystals have the form of blue vitriol and contain five molecules of water.

Through the isomorphism of the double potassio-sulphates, the iron-copper group of metals is connected with the zinc group previously described.

SILVER is a metal having a familiar white lustre, and is very malleable and ductile. It may be obtained in leaves so thin as to transmit light of a bluish-green colour, similar to that which passes through gold leaf and films of copper. It is worthy also of notice that the light reflected from silver is not quite white, but assumes a close resemblance to the colour of copper after repeated reflection. Silver melts at about 950°, and it passes off in blue vapour at the temperature of the oxyhydrogen flame. It is the best conductor of heat and electricity. It is undoubtedly related to the metals of the alkalies, for its chloride is isomorphous with sodium chloride, its sulphate is isomorphous with anhydrous sodium sulphate, and by combination with aluminium sulphate it yields a true alum which crystallises in octahedrons. In almost every other respect, however, it differs from them.

Pure silver has the singular property of dissolving, when fused in the air, a considerable volume of oxygen, which escapes as the temperature goes down and the metal solidifies. This phenomenon does not appear to be connected with the production of an oxide. Silver has no action upon water or steam at any temperature, and is

quickly reduced from its salts by zinc, iron, or even mercury. Under certain circumstances some reducing agents throw down from solutions of silver salts precipitates which when dry assume various colours. One variety resembles gold. These substances are supposed to consist of allotropic modifications of the metal, but they always contain a considerable quantity of non-metallic matter, and further investigation is very desirable.

The ordinary oxide of silver, Ag_2O, is said to be sufficiently soluble in water to give a faintly alkaline reaction, but it differs entirely from potash or soda in appearance and in its decomposability by heat. The chloride, iodide, sulphide, carbonate, and phosphate of silver are all insoluble in water, and the sulphate very sparingly soluble.

Silver forms a peroxide, Ag_2O_2, even less stable than the potassium peroxide. There is also a peroxide, Ag_4O_3, the composition of which is, however, not very well established.

The relations of silver to the alkali metals on the one hand, and to copper on the other, are about equally distant.

The position of silver in regard to sodium on the one hand, and to copper on the other, is not unlike that of thallium in respect to potassium, rubidium, and cæsium and to lead.

METALS.—9. PLATINUM GROUP.

SUB-GROUP A.—GOLD.

Triad. Salt types $(\overset{\prime\prime}{M_2})Cl_2$ *and* $\overset{\prime\prime\prime}{M}Cl_3$.

Gold is a metal of familiar yellow colour and high density. In consideration of its inalterability in the fire or by the action of acids (save nitro-muriatic acid, hence called *aqua regia*), gold was regarded by the old chemists as the type of a 'noble' metal. It forms two classes of salts, of which the aurous are somewhat unstable, readily undergoing

decomposition into an auric compound and metallic gold. The sodio-aurous thiosulphate $\left.\begin{matrix}Na_6\\Au_2\end{matrix}\right\}(S_2O_3)_4.4H_2O$ is one of the most definite.

The trichloride is the most important auric compound. It is a red, crystalline, deliquescent body, which forms yellow crystallisable compounds with the chlorides of hydrogen and the alkali-metals, $HAuCl_4$, $KAuCl_4$, NH_4AuCl_4, &c.

Gold is reduced from its solutions with the greatest readiness by nitrous acid, sulphurous acid, ferrous salts, and all reducing agents, including many organic substances. Its oxides and chlorides also yield up the metal when strongly heated.

Sub-group B.

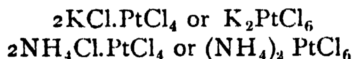
The members of this group range themselves very naturally into two divisions, each of which exhibits a striking uniformity of atomic weight and density. With one of these gold allies itself, in virtue of its high density and atomic weight, as well as its resistance to oxidation and solution in acids; also by the yellow colour of its compounds and the tendency of its highest chloride to form double salts. With the other, silver is, perhaps, in a similar manner, remotely connected, though in this case it must be admitted there is but little in the properties of the metal to sanction such an arrangement.

	Symb.	At. Wt.	Dens.		Symb.	At. Wt.	Dens.
Silver *Monad*	Ag	107·93	10·5	Gold *Triad*	Au	197	19·3
Palladium	Pd	106	11·5	Platinum	Pt	194·8	21·5
Rhodium	Ro	103	12·0?	Iridium	Ir	193	22·4
Ruthenium *Tetrad*	Ru	101·7	12·0?	Osmium *Tetrad*	Os	191	22·5

The true platinum metals are white metals which require for their fusion the highest attainable temperatures of the oxyhydrogen flame. It is stated, indeed, that osmium has never been really melted ; hence the numbers by which their respective densities are denoted can only be approximately correct.

They differ somewhat in their behaviour towards reagents. Palladium, for example, is slowly dissolved by nitric acid, while some of the others resist the action even of *aqua regia*. Ruthenium and osmium, on the other hand, although slowly attacked by *aqua regia* when in the compact state, undergo oxidation somewhat rapidly when heated in the air.

They all, with the exception of rhodium, form more or less stable tetrachlorides, which are generally yellow and easily reducible by heat, either to lower chlorides or to the metallic state. These compounds also unite with hydrogen chloride and with the chlorides of the alkali-metals, forming crystallisable salts, which in some cases, as, for example, the platinichlorides of potassium and ammonium,



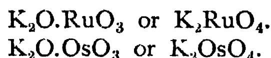
$$2KCl.PtCl_4 \text{ or } K_2PtCl_6$$
$$2NH_4Cl.PtCl_4 \text{ or } (NH_4)_2 PtCl_6$$

are but slightly soluble in water and are highly characteristic. But beside these tetrachlorides, the platinum metals yield dichlorides and sesquichlorides, which are in special cases of greater importance. The dichloride of palladium, for example, is one of its most important compounds, and far more stable than the tetrachloride, which is known only in a state of solution, and in its double salts. Rhodium, again, forms only one chloride, and that the sesquichloride.

The following are all the definite chlorides of these metals which have been described :—

Dichlorides.	Sesquichlorides.	Tetrachlori
$PdCl_2$	—	$PdCl_4$
$PtCl_2$	—	$PtCl_4$
—	Ro_2Cl_6	—
$IrCl_2$?	Ir_2Cl_6	$IrCl_4$
$RuCl_2$	Ru_2Cl_6	—
$OsCl_2$	Os_2Cl_6	$OsCl_4$

Ruthenium and osmium are specialised by the existence of potassium salts called ruthenate and osmiate, which contain the elements of potassium oxide, together with a trioxide of ruthenium or osmium.



$K_2O.RuO_3$ or K_2RuO_4.
$K_2O.OsO_3$ or K_2OsO_4.

The trioxides, or anhydrides, are not known in an isolated state. But the most remarkable compounds of these metals are the tetroxides RuO_4, OsO_4, which are highly volatile bodies, soluble in water to form acid solutions, but apparently incapable of generating salts. The constitution of these compounds is not well understood. They are the only metallic tetroxides known.

CHAPTER XIII.

THE PERIODIC SYSTEM.

THROUGHOUT the preceding chapters, in which the classification of the elements and of their compounds has been discussed, frequent reference has been made to the remarkable relations which are observable in the numerical value

of the atomic weights. These relations have from the first offered to chemists an attractive problem, the importance of which has greatly increased within the last few years.

Very early in the history of modern chemistry, namely, in the year 1815, the hypothesis was put forward by Dr. Prout that, taking the atomic weight of hydrogen as 1, the atomic weights of all the remaining elements are multiples of this by a whole number. This hypothesis, either in its original form or modified subsequently by the assumption of the value ·5 or ·25 for the atomic weight of hydrogen, has not stood the test of rigorous experimental investigation. But within the last few years a further modification of Prout's hypothesis has attracted attention in connection with speculations relating to the genesis of the so-called elements, based upon the fundamental idea that these bodies were formed in the beginning by the condensation or polymerisation of the primordial simple matter which is supposed to have pervaded all space.

Independently of such considerations, however, the relations which have been discovered to subsist between the atomic weights of the elements and the properties of these substances and of their compounds have been made the basis of a system of classification which has been almost universally adopted by chemists. A short account of some of the most interesting of these observations will now be laid before the student.

A relation which is conspicuous among the atomic weights of the best known elements has already been frequently adverted to in previous pages. It is this. Many closely related elements may be ranged in short series of three, in which a gradual modification of properties is observable in tracing the series through its successive terms. In such series the atomic weight of the intermediate term is generally very nearly the half of the sum of the atomic weights of the extremes.

Such an agreement is shown, for example, in the case of the alkali metals, lithium, sodium, and potassium.

Atomic weight of lithium	=	7·03
" " sodium	=	23·05
" " potassium	=	39·15

And $\frac{7{\cdot}03 + 39{\cdot}15}{2} = 23{\cdot}09.$

In a few cases the atomic weights of elements which are associated together by reason of their chemical characteristics are simple multiples one of another, as in the example of oxygen, whose atomic weight is 16, whilst that of sulphur is approximately 32, or they have nearly the same value, as in the case of iron and manganese, nickel and cobalt.

These considerations have been very ably discussed by several chemists, but especially by Dumas, who pointed out, more than half a century ago, that one of the most interesting relations among the atomic weights of the elements may be expressed somewhat as follows. The numbers representing the atomic weights of a series of closely allied elements, when written down in the order of their numerical value, represent an arithmetical progression which may be expressed by a common formula,

$$a + nd,$$

in which a is the first term and d the difference in passing from term to term. Thus, for example, the series of alkali metals conforms to this type:

$$a = 7 \qquad d = 16$$

Atomic weight of lithium	$= a$	=	7
" " sodium	$= a + d$	=	23
" " potassium	$= a + 2d$	=	39

Now it is obvious that this relationship is just that which

obtains in the combining values of the several members of a homologous series. The radicles of the series to which common alcohol belongs, for example, run in the following order, where $a = 15$ and $d = 14$:

Methyl	CH_3	$= 15$	$= a$
Ethyl	C_2H_5	$= 29$	$= a + d$
Propyl	C_3H_7	$= 43$	$= a + 2d$
Butyl	C_4H_9	$= 57$	$= a + 3d$
Amyl	C_5H_{11}	$= 71$	$= a + 4d$
&c.	&c.	&c.	&c.

Such a series also exhibits several of the peculiarities already pointed out in several families of elements. Thus, taking three contiguous terms or three terms at equal intervals in the series, the middle one has a combining weight equal to half the sum of the combining weights of the two extreme terms. Thus:

$$\frac{CH_3 + C_3H_7}{2} = \frac{15 + 43}{2} = 29 = C_2H_5.$$

Moreover in the higher members of such a series numbers such as 141 and 281, 127 and 253, 113 and 225 occur, and it may be argued that if these radicles were elementary or if their composition were unknown, such numbers might fairly be considered as really representing a ratio of 1 : 2.

This simple formula, however, is only approximately applicable to a few of the elementary series, and in many cases it is necessary to recognise a more complex expression, which may be written

$$a + nd + nd' + nd'' + \ldots .$$

in which a represents the fundamental characteristic of the series, and d, d', d'', &c., the differences.

An example will render its application easily intelligible.

General Formula.

First	term	a
Second	,,	$a + d$
Third	,,	$a + 2d + d'$
Fourth	,,	$a + 2d + 2d' + d''$

NUMERICAL VALUES.

First	term	19		= F
Second	,,	19 + 16·45	= 35·45	= Cl
Third	,,	19 + 32·9 + 28·06	= 79·96	= Br
Fourth	,,	19 + 32·9 + 56·12 + 18·83	= 126·85	= I

Here if $d'' = a$ the fourth term becomes

$$2a + 2d + 2d' = 127{\cdot}02.$$

A similar general formula will be found to apply to the series N, P, As, Sb, Bi.

It is obvious, however, that the sum of such a series can only be made to coincide with the exact value of the atomic weight by adjustment of the differences.

In the year 1866 a remarkable observation was made by J. Newlands, to the effect that when the elements are arranged in a continuous series in the order of their atomic weights, commencing with hydrogen, there is at equal intervals in the series a recurrence of the same or similar general characters, both physical and chemical. This *periodic* revival of characteristics occurs, with a few exceptions, at about every eighth member of the series, as will presently be shown. This discovery has been elaborately studied by Mendeléeff and Lothar Meyer, and that which has long been vaguely recognised is now fully established, namely, that the properties of the elements stand in a definite relation to their atomic weights. Further, if we write down a few of the best known elements in the order indicated, and add the formulæ of some of their most characteristic

compounds, the reader who has carefully studied their properties will recognise at once the existence of some kind of periodic relation.

Element.	Atomic weight.	Relative density.	Atomic volume.[1]	Chief chloride.	Chief hydride.	Chief oxide.
Li . .	7·03	·578	12	LiCl	?	Li_2O
Be . .	9·1	1·64	5·6	$BeCl_2$	?	BeO
B . .	11	2·68	4·1	BCl_3	BH_3	B_2O_3
C (Graphite)	12	2·2	5·4	CCl_4	CH_4	CO_2
N . .	14·04			NCl_3	NH_3	N_2O_5
O . .	16	Liq. ·99	16	OCl_2	OH_2	
F . .	19				FH	
Na . .	23·05	·97	23	NaCl	?	Na_2O
Mg . .	24·36	1·7	14	$MgCl_2$	?	MgO
Al . .	27·1	2·6	10	$AlCl_3$	?	Al_2O_3
Si . .	28·4	2·49	11	$SiCl_4$	SiH_4	SiO_2
P . .	31	2·1	14	PCl_3 & PCl_5	PH_3	P_2O_5
S . .	32·06	2·07	16	SCl_2 & SCl_4	SH_2	SO_3
Cl . .	35·45	Liq. 1·38	25		ClH	ClO_2
K . .	39·15	·865	45	KCl	?	K_2O
Ca . .	40	1·8	22	$CaCl_2$	?	CaO

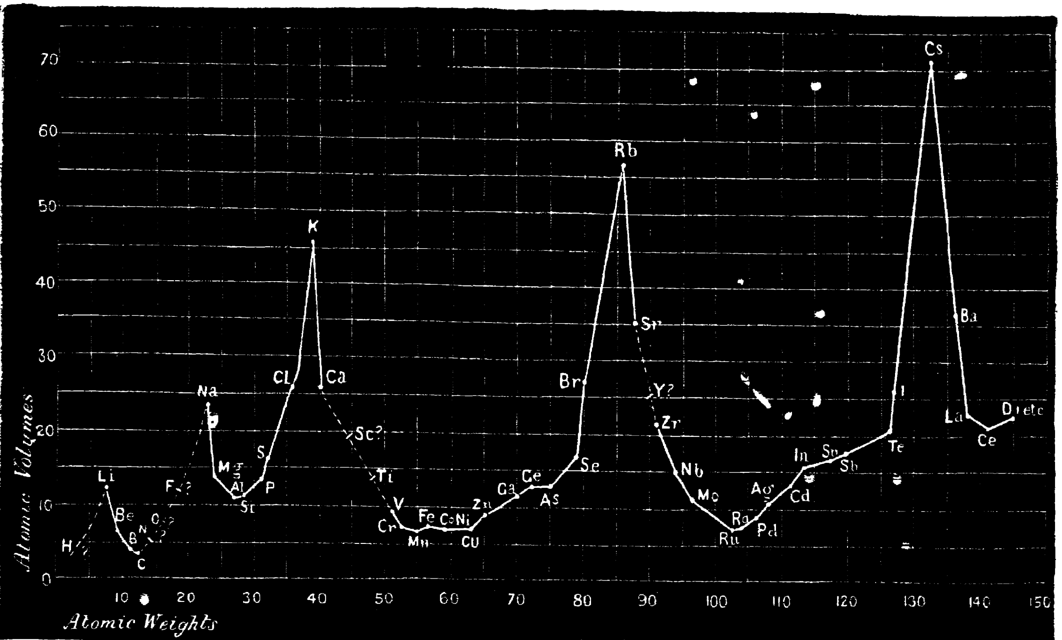
The gradual waxing and waning of density and atomic volume, of valency, of disposition to combine with chlorine and with hydrogen, and the basylous or acidulous character of the oxides of these elements may be displayed more conspicuously by a graphic construction such as the following (p. 234).

Here the curve is traced by the intersection of horizontal lines, whose length is proportional to the atomic weights, and vertical lines, which indicate the atomic volumes. It is certainly remarkable that the atomic volume should not increase with the atomic weight in the same or nearly

[1] The volume of an atom of an uncombined element in a liquid or solid state is assumed to be in direct proportion to the atomic weight, and inversely as the density of the substance: hence *atomic volume* is an abbreviated expression meaning the quotient obtained by dividing the atomic weight by the density.

the same ratio, but should thus increase and diminish in value at pretty regular intervals, but the regularity with which these alternations are followed by the various physical and chemical characters of the elements is still more interesting. The student will recognise without difficulty such facts as the following by reference to the diagram.

It will be seen first that, passing from left to right, the ascending parts of the curve are occupied by elements the electro-negative character of which becomes more and more pronounced the higher they stand, while on each summit and the succeeding declivity are stationed elements of electro-positive character which becomes less marked as we go downwards. The elements which are to be found upon the elevated portions of the curve, and which therefore have the largest atomic volume, habitually behave more energetically as chemical agents than those which occupy the lower portions. And this general inference is supported by reference to the heats of formation of the chlorides or oxides of the elements in question. On the ascending portions of the curve, including the topmost points, are also found the volatile and fusible elements, while those which occur at the lowest parts are substances which are, for the most part, fusible and vaporisable only with difficulty. Malleability and ductility and other physical properties are also exhibited periodically at successive points upon the curve. Moreover, it has been found that the properties of the corresponding compounds of the elements, so far as they can be at present traced, exhibit a similar periodic character. Thus the melting points of the normal chlorides of the elements, when set out graphically in the manner shown in the case of the atomic volumes, give a curve which exhibits the same general characters, consisting of alternate elevations and depressions which correspond roughly with those shown in the diagram. The corresponding bromides and iodides also give similar curves, following pretty closely the curve of the chlorides.


Atomic Volumes
Atomic Weights
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
H
Li
Be
B
N
C
O?
F?
Na
Mg
Al
Si
P
S
CL
K
Ca
Sc?
Ti
V
Cr
Mn
Fe
CoNi
CU
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y?
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Di etc

The only character of importance which does not exhibit alternate maxima and minima is specific heat. This, however, though not periodic with increase of atomic weight, is somewhat dependent upon atomic volume, for it will be noticed by reference to the diagram that those elements which do not closely conform to the law of Dulong and Petit have not only a small atomic weight, but small atomic volume.

The table given on p. 236, contains the elements arranged in a manner slightly modified from that proposed by Mendeléeff. It will be noticed, that the vertical columns contain closely related elements in two parallel series, the members of which alternate in the value of their atomic weights. The first six horizontal lines are now nearly complete, but there are many gaps lower down. It is interesting to notice that the metals gallium, discovered in 1875, and germanium, in 1886, have been found to fill two places previously vacant, and that they present nearly all the characters belonging to the position which, in virtue of their atomic weights, they hold in the system.

The true places of the rare metals, neodymium, terbium, thulium, samarium, ytterbium are still unsettled, as well as those of several other elements which are associated with the yttrium-cerium groups, but which are at present distinguishable only by spectroscopic characters.

The table requires a few remarks. The first series consists of elements which, though often spoken of as typical, are entitled to be so regarded only in a limited sense. While there is considerable agreement in regard to properties between lithium and sodium on one side and between fluorine and chlorine on the other, the element which stands at the head of each of the intermediate groups is followed by one which is very different in all its more obvious properties. The differences, for example, between oxygen and sulphur and between nitrogen and phosphorus are more strongly marked than their resemblances, and there

Supplementary. Valency various.	Group I. Monads RCl R_2O	Group II. Diads RCl_2 RO	Group III. Triads RCl_3 R_2O_3	Group IV. Tetrads RH_4 RO_2	Group V. Triads or pentads RH_3 R_2O_5	Group VI. Diads or Hexads RH_2 RO_3	Group VII. Monads or Triads RH	Supplementary. Valency O
H 1·01*							(−focus)	He 4
	Li 7·03	Be 9·1	B 11	C 12	N 14·04	O 16	F 19	Ne 20
	Na 23·05	Mg 24·36	Al 27·1	Si 28·4	P 31	S 32·06	Cl 35·45	A 40
	K 39·15	Ca 40	Sc 44·1	Ti 48·1	V 51·2	Cr 52·1		
Mn 55 } Ni 58·7 } Cu 63·6 Fe 56 } Co 59 }		Zn 65·4	Ga 70	Ge 72	As 75	Se 79·1	Br 79·96	Kr 82
	Rb 85·4	Sr 87·6	Y 89	Zr 90·6	Nb 94	Mo 96		
Ru 101·7 } Pd 106 Rh 103 } Ag 107·93		Cd 112	In 114	Sn 118·5	Sb 120	Te 127	I 126·85	X 128
	Cs 133	Ba 137·4	La 138	Ce 140	Pr 141 ?			
Os 191 } Pt 194·8 Au 197·2 Ir 193 }	(+ focus)							
					Ta 183	W 184		
		Hg 200·3	Tl 204·1	Pb 206·9	Bi 208·5			
				Th 232		U 239·5		

* The ratio of the atomic weight of oxygen to that of hydrogen is 15·88 to 1, or approximately 16 to 1·01. It will be remembered that as explained in Chapter III., if the atomic weight 16 is adopted for oxygen the atomic weights of many other elements come much nearer to whole numbers than when the values 15·88 for oxygen and 1 for hydrogen are employed. The atomic weights inserted in the table are on the scale of 16 for O, and this involves the adoption of a number for hydrogen greater than 1, approximately 1·01.

is nothing corresponding to the close relationship noticeable among the members of the several triplets Cl—Br—I, S—Se—Te, &c., which follow.

The whole of the non-metallic elements are included in a region which occupies the upper right-hand corner of the table, and is marked off by the dotted line. All to the left of this are positive, and with the exception of hydrogen present metallic characters more or less distinctly.

In tracing the groups downwards in the several vertical columns it will be found that on the negative side the negative character is gradually reduced as the atomic weight increases, and in some cases, as in the P—As—Sb—Bi group, the negative is gradually exchanged for a positive character. On the positive side the positive characteristics and chemical activity increase with rise of atomic weight. This difference is apparently connected with atomic *volume*, for by reference to the curve (p. 234) it will be noticed that while there is considerable increase in atomic volume in passing from Li to Cs, the atomic volumes of Cl, Br, I are nearly equal.

In many cases in passing vertically downwards a tendency will be noticed to the gradual production of a new type of compounds, the formation of which depends upon a different, usually a lower, rate of valency. For example, magnesium forms but one series of salts represented by the chloride $MgCl_2$, while mercury gives both mercurous and mercuric compounds Hg_2Cl_2 and $HgCl_2$. Aluminium forms only one series of salts and those typified by the trichloride $AlCl_3$. Thallium, however, forms a series of thallous compounds TlCl, &c., which are much more stable than the thallic compounds TCl_3, &c. Similar remarks apply to other cases, as may be seen by comparing the relative stability of lead dichloride and lead tetrachloride, of bismuthous oxide and bismuthic oxide, with the habit of the group at the extremity of which they stand.

The table as a whole brings out clearly enough the

principle of the dependence of properties on atomic weight and the generally periodic character of the changes which follow the gradual increase of atomic weight. It presents, however, many difficulties and anomalies, the existence of which shows that the true relation between atomic weight and properties remains to be discovered. One of the greatest difficulties occurs in assigning to the newly discovered argon group a place in the system. In the table a place is given to them provisionally outside the negative groups and parallel with them. If the table were wrapped round a cylinder with axis parallel to the vertical columns of the table, the argon group would divide the positive side from the negative, forming a sort of neutral or transition group.

It is also obvious that such relations as are known to subsist between thallium and the alkali group, and between lead and barium, are neither accounted for nor indicated by their position. The metals manganese, iron, nickel, cobalt, and copper again are connected by isomorphism with magnesium and zinc, but a strict application of the periodic principle allows no place for them near to those metals, and a similar difficulty occurs in the case of the metals of the platinum group.

To the student the table will be found useful as an aid to the memory, but what is to be inferred from the relations which have been pointed out as regards the possibility of a common origin of these undecomposible forms of matter or as to a common constituent or constituents must be considered as an open question, which will probably remain unanswered for some time to come.

CHAPTER XIV.

ACIDS, BASES, SALTS.

CHEMICAL compounds are divisible broadly into two great classes, namely, electrolytes and non-electrolytes. The former, when dissolved in a suitable liquid, are capable of conducting an electric current, and are thereby resolved into positive and negative constituents, as already explained (Chap. X.).

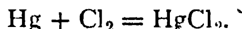
Compounds of this class, consisting of a positive ion united to a negative ion (see Chap. XIX.), receive the name *acid*, *base*, or *salt*, according to the properties they exhibit. A study of their modes of formation, their properties, and characteristic reactions shows that they all possess fundamentally the same constitution and may be described as *salts*. The application of the term 'salt' was formerly restricted to compounds which resemble in external appearance, crystalline character, solubility, and taste, common salt, a substance originally obtained from sea water. The word is derived from the Greek ἅλς (fem.), the sea, and hence ἅλς (masc.), salt derived from the sea, and it appears in nearly the same form in many languages—*e.g.* *sal* (Latin), *sel* (French), *salz* (German). Liquid and solid, soluble and insoluble compounds are now alike included under the term salt, and physical characters alone afford no basis for a definition.

A salt may now be defined as a substance which in the liquid state or dissolved in certain liquids, especially water, behaves as an electrolyte, and is also resolvable by double interchange with other compounds into a positive and a negative constituent. It is customary to reserve the name salt for compounds in which the positive element consists wholly or partly of a metal or pseudo-metal, while the compounds in which the positive constituent is wholly hydrogen

are called acids, and those in which a metal is combined with hydroxyl are often called bases, or better, basic hydroxides. It will be convenient to consider these three classes of compounds separately.

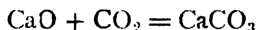
Salts.—Metallic salts may be formed in a variety of ways, among which the following are the most important :—

(*a*) Union of elements :—

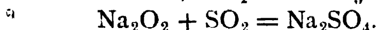


$$Hg + Cl_2 = HgCl_2.$$

(*b*) Union of metallic and non-metallic oxides :—



$$CaO + CO_2 = CaCO_3$$



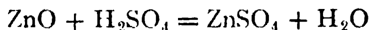
$$Na_2O_2 + SO_2 = Na_2SO_4.$$

(*c*) Action of metal on acid :—

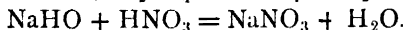


$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

(*d*) Action of metallic oxide or hydroxide on acid :—

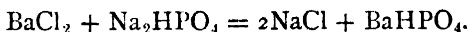


$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$



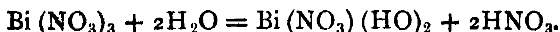
$$NaHO + HNO_3 = NaNO_3 + H_2O.$$

(*e*) Double decomposition between two pre-existent salts :—



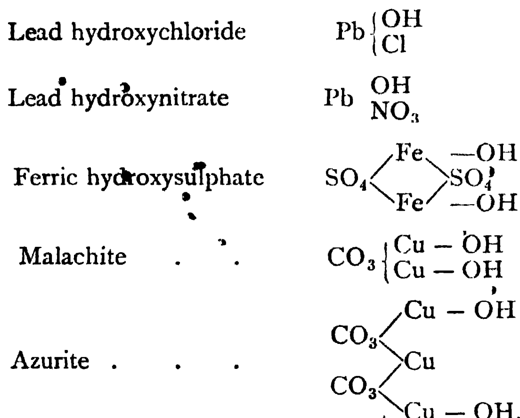
$$BaCl_2 + Na_2HPO_4 = 2NaCl + BaHPO_4.$$

When a salt is dissolved in water two kinds of change may occur. It will be dissociated into its ions to an extent which varies in each case and which is dependent upon its nature and composition. It may be also partly or completely resolved by the chemical action of the water into an acid and a hydroxide, or basic salt. Such a process is called hydrolysis. Its effects become visible when either of these products is insoluble, or only slightly soluble, in the liquid. An example is provided by the action of water on bismuth nitrate :—



$$Bi(NO_3)_3 + 2H_2O = Bi(NO_3)(HO)_2 + 2HNO_3.$$

Compounds such as these are often called basic salts. The following are some additional examples :—



In consequence of the hydrolytic effect of water on many salts, their solutions sometimes exhibit unexpected characters. For example, common sodium phosphate, Na_2HPO_4, is decidedly alkaline to test paper notwithstanding its apparently acid constitution. This arises from the action of the water, which resolves it partly into a mixture of caustic soda with the monosodium salt :—

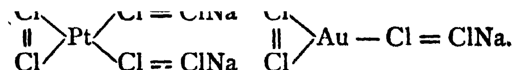


$$Na_2HPO_4 + H_2O = NaHO + NaH_2PO_4.$$

Similarly potassium cyanide, a compound which, when dry, bears fusion without suffering decomposition, when dissolved in water gives a strongly alkaline liquid, owing to the formation of potassium hydroxide mixed with prussic acid, which is a very weak acid.

In the production of salts the combining capacity of the materials is usually regarded as exhausted, the affinity of the sodium in common salt, for example, being satisfied by the equal and opposite affinity of the chlorine. It is

evident, however, that in a great many cases, perhaps in all, there is a reserve of combining power and of potential energy, for nearly all salts under suitable conditions are capable of entering into combination in definite proportions with water, alcohol, ammonia, and with other salts. Water of crystallisation has already been referred to (p. 167). Double sulphates and double chlorides, &c., are probably to be accounted for by an extension of the same hypothesis (see p. 159). Sodium chloroplatinate and chloraurate might, for example, be expressed by the following formulæ :—



Acids.—Acids are salts of hydrogen. They are distinguished from metallic salts in general by greater chemical activity, being capable of producing, for example, hydrolytic effects more readily. They are also characterised by well-known behaviour with certain dyes, such as litmus. The sour taste of diluted acids is a common property, but is not more remarkable than the bitterness of magnesium, the astringency of iron, and the sweetish taste of lead salts.

It has already been pointed out that many acids are crystalline, and in all external characters resemble salts of metals (p. 184). The part played by oxygen in relation to acidity also has been discussed (p. 162). The modern hypothesis by which the chemical activity of an acid is connected with its specific capacity for electrolytic decomposition will be explained in a future chapter. It will be sufficient to say for the present that hydrogen is the characteristic element of all acids, and that to the readiness with which most acids undergo ionisation and the mobility of the hydrogen ion they probably owe their activity as chemical agents.

It now remains only at this point to give an account of the

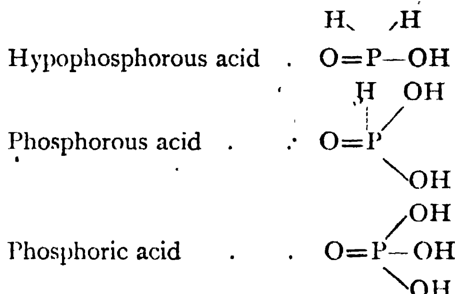
property of acids known as 'basicity.' This inquiry amounts in some cases to a determination of the weight of the molecule, and reference has already been made to examples of the kind in the chapter on Molecular Weights (p. 95). The question is, however, one of great importance, and deserves to be examined a little more in detail. The basicity of an acid depends upon the number of atoms of hydrogen directly exchangeable out of each molecule for metallic atoms; an acid containing one such atom of hydrogen being called monobasic, one containing two such atoms is dibasic, or three tribasic, and so on. We may infer the basicity of a given acid from the number of distinct salts it is capable of yielding with each metal. Monobasic acids generally give one salt, dibasic acids, as shown in the case of sulphuric acid, give two, and tribasic acids give three. Mere inspection of the formula of an acid does not, however, furnish sufficient information upon which to form a judgment regarding the basicity of the acid and the number of salts it is capable of producing; for it by no means follows, from the existence of two or three atoms of hydrogen in the molecule, that it should be dibasic or tribasic. The basicity depends not upon the total number of hydrogen atoms present, but upon the total number endowed with this particular power of exchange.

The three following acids of phosphorus afford an example of this. Each molecule contains three atoms of hydrogen, but the first is monobasic, the second dibasic, the third tribasic:—

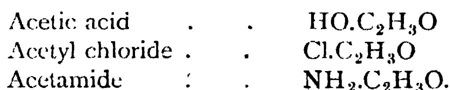
Hypophosphorous acid .	H_3PO_2 or HPH_2O_2
Phosphorous acid . .	H_3PO_3 or H_2PHO_3
Phosphoric acid . .	H_3PO_4

In this and similar cases it has been generally observed that increase of basicity, as well as of sourness and general chemical acidity, accompanies the addition of oxygen. Hence it has been inferred that those atoms of hydrogen

which are exchangeable for metals are combined more intimately with oxygen than others which are not similarly exchangeable. On this hypothesis the formulæ of the three acids referred to above are represented in the following manner :—



But acids are capable of undergoing a variety of modifications under the influence of reagents, and some of these are available as evidence towards the establishment of their basicity. It has been found, for example, that acids which possess only one basic atom of hydrogen, or are monobasic, yield only one amide and one chloride. Acetic acid, for example, gives the following derivatives, the relation of which to acetic acid is obvious from the formulæ —



Acetic acid . .	$HO.C_2H_3O$
Acetyl chloride . .	$Cl.C_2H_3O$
Acetamide . .	$NH_2.C_2H_3O$.

Dibasic acids give two derivatives of the same kind, and tribasic acids give three.

We may now resume the case of sulphuric acid, already adverted to (p. 95), as a very instructive example.

The simplest formula for sulphuric acid is H_2SO_4. The problem before us is to prove that this formula, with the relative weight 98, is the formula of the molecule, and that the acid is dibasic.

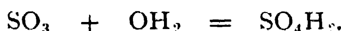
1. The fact of the existence of two classes of sulphates has been already appealed to. It is clear that the whole of the hydrogen of the acid is replaceable by metals, and that it is capable of replacement one half at a time. We arrive then at such formulæ as these :—



$$\left.\begin{matrix}Na\\H\end{matrix}\right\}SO_4 \qquad \left.\begin{matrix}Na\\Na\end{matrix}\right\}SO_4 \qquad \left.\begin{matrix}K\\K\end{matrix}\right\}SO_4 \qquad \left.\begin{matrix}K\\Li\end{matrix}\right\}SO_4$$

Evidence of this kind is almost conclusive, but it happens that in the present instance other testimony is abundant.

2. Thus we might show that sulphuric acid is produced when sulphur trioxide and water, both bodies of known molecular weight, unite together—



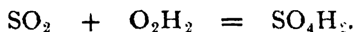
$$SO_3 + OH_2 = SO_4H_2.$$

3. Also when sulphur dioxide is dissolved in water and the solution exposed to contact with oxygen—



$$SO_2 + OH_2 + O = SO_4H_2.$$

4. It is also formed by the direct union of hydrogen peroxide and sulphur dioxide—



$$SO_2 + O_2H_2 = SO_4H_2.$$

A sulphate being generated in the following strictly parallel case of combination—



$$SO_2 + PbO_2 = SO_4Pb.$$

5. Sulphuric acid is generated by the decomposition of sulphuryl chloride by water—



$$SO_2Cl_2 + 2H_2O = SO_4H_2 + 2HCl.$$

According to equations 2, 3, 4, the whole of the acting materials enter into the composition of the sulphuric acid which is produced, and therefore there is a strong probability in favour of the molecular weight of sulphuric acid

being the sum of their separate molecular weigths. Similar considerations apply to equation 5. The molecule of sulphuric acid is here shown to be built up of the molecules of the sulphur oxychloride and water, minus two atoms of hydrogen and two atoms of chlorine.

6. We now come to some reactions in which various constituents of the sulphuric acid molecule are replaced. When the acid is heated with phosphoric chloride, two successive reactions of the same kind ensue. In the first an atom of chlorine is introduced in place of the group (OH) which is removed.



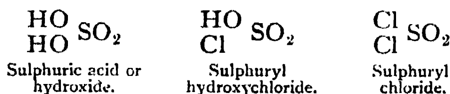
$$H_2SO_4 + PCl_5 = HClSO_3 + POCl_3 + HCl.$$

The compound $HClSO_3$ then interacts with itself, if the temperature is sufficiently high, reproducing sulphuric acid and a new chloride, thus :



$$2HClSO_3 = H_2SO_4 + SO_2Cl_2.$$

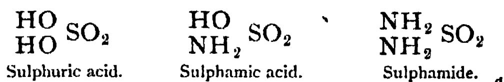
The relation of the two new chlorides to sulphuric acid may be exhibited most satisfactorily by writing the formulæ in the following manner :—



$$\begin{matrix} HO \\ HO \end{matrix} SO_2 \qquad \begin{matrix} HO \\ Cl \end{matrix} SO_2 \qquad \begin{matrix} Cl \\ Cl \end{matrix} SO_2$$

Sulphuric acid or hydroxide.	Sulphuryl hydroxychloride.	Sulphuryl chloride.

7. Two 'amides,' standing in the same kind of relationship towards sulphuric acid, also exist. Their formulæ may be written thus : —



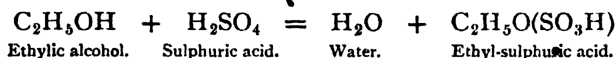
$$\begin{matrix} HO \\ HO \end{matrix} SO_2 \qquad \begin{matrix} HO \\ NH_2 \end{matrix} SO_2 \qquad \begin{matrix} NH_2 \\ NH_2 \end{matrix} SO_2$$

Sulphuric acid.	Sulphamic acid.	Sulphamide.

The existence of these compounds and the corresponding chlorides supplies evidence similar to that deducible from a knowledge of the acid and double sulphates (1). These facts tend to show that the hydrogen contained in a molecule of sulphuric acid is divisible into two equal parts,

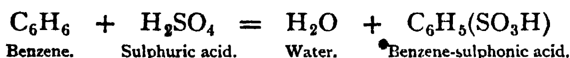
and that these two hydrogen atoms are probably more closely united with two atoms of oxygen than with other constituents of the molecule.

8. When concentrated sulphuric acid is made to act on certain hydrocarbons, alcohols, phenols, and other bodies, compounds are produced which have the properties of monobasic acids. These compounds are in some degree analogous to salts; at any rate, sulphuric acid could not produce derivatives of this kind if it did not contain at least two atoms of basylous hydrogen.



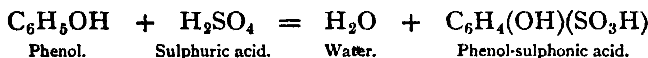
$$C_2H_5OH + H_2SO_4 = H_2O + C_2H_5O(SO_3H)$$

Ethylic alcohol. Sulphuric acid. Water. Ethyl-sulphuric acid.



$$C_6H_6 + H_2SO_4 = H_2O + C_6H_5(SO_3H)$$

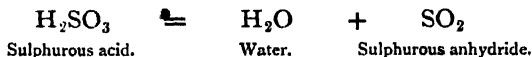
Benzene. Sulphuric acid. Water. Benzene-sulphonic acid.



$$C_6H_5OH + H_2SO_4 = H_2O + C_6H_4(OH)(SO_3H)$$

Phenol. Sulphuric acid. Water. Phenol-sulphonic acid.

In one respect, which has not yet been referred to, there is a difference between acids which contain oxygen and those which do not contain that element. Compounds in which there is no oxygen cannot by any possibility be made to yield water. Hence there are no anhydrides corresponding to the haloid acids. Oxyacids, however, may, in various ways, be made to furnish water and an oxide, which is called an *anhydride*. Thus sulphurous acid splits up readily in the following manner:—



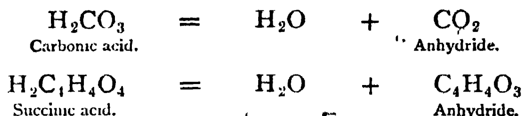
$$H_2SO_3 \rightleftharpoons H_2O + SO_2$$

Sulphurous acid. Water. Sulphurous anhydride.

Dibasic acids give their anhydrides most readily when simply heated, whereas monobasic acids generally require to be treated with some dehydrating agent. This is probably connected with the fact that a dibasic acid always contains within itself the elements of water, whilst a mono-

basic acid cannot generate water except by the combined action of two molecules.

Dibasic.



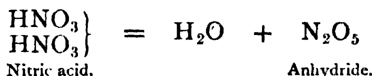
$$H_2CO_3 = H_2O + CO_2$$

Carbonic acid. Anhydride.

$$H_2C_4H_4O_4 = H_2O + C_4H_4O_3$$

Succinic acid. Anhydride.

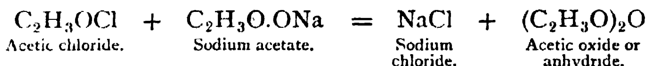
Monobasic.



$$\left.\begin{matrix} HNO_3 \\ HNO_3 \end{matrix}\right\} = H_2O + N_2O_5$$

Nitric acid. Anhydride.

In the case of some monobasic acids, the anhydride can only be obtained by a succession of operations. In order to prepare acetic anhydride, for example, the chloride is first made from the acid, and this compound is then allowed to react upon a salt.



$$C_2H_3OCl + C_2H_3O.ONa = NaCl + (C_2H_3O)_2O$$

Acetic chloride. Sodium acetate. Sodium chloride. Acetic oxide or anhydride.

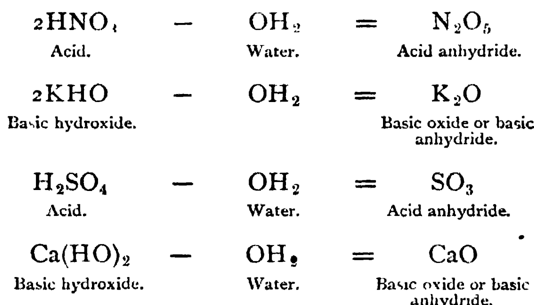
Bases.—The word *base* belongs to the obsolete dualistic theory of salts. According to this theory, every salt was supposed to be made up of two parts, one of which, consisting of a metallic oxide, formed the base; whilst the other part, usually the oxide of a non-metal, or some group consisting of carbon, hydrogen, and oxygen, was regarded as the acid. Sulphate of soda, for example, was, according to dualistic phraseology, composed of the base soda or oxide of sodium, and sulphuric acid or trioxide of sulphur, and its formula was written $NaOSO_3$, or, adopting modern atomic weights, Na_2OSO_3.

This idea has been considerably modified, and the oxides of which the elements are present in such a salt as sodium sulphate are no longer supposed to exist in the compound in a semi-independent condition. The *primary*

products of electrolysis of ordinary salts are now known to be hydrogen or a metal at the negative, and a non-metal alone or associated with oxygen at the positive electrode. When sodium sulphate or any alkaline salt is electrolysed the products which appear at the electrodes are respectively an alkali and an acid, and this fact appeared to Berzelius and the chemists of his time to support the view of saline constitution explained above. This alkali and acid are, however, secondary products, the result of the liberation of the positive and negative ions of the salt in the presence of water.

The hydroxides and the lower oxides of metals agree in the property of reacting with acids with the production of salts and water.

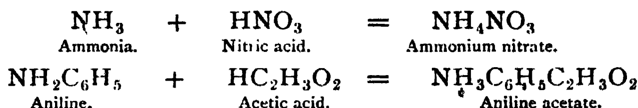
It will be noticed that a basic hydroxide and basic oxide have the same relation to each other as an acid and its anhydride. For example—



$2HNO_3$ Acid.	−	OH_2 Water.	=	N_2O_5 Acid anhydride.
$2KHO$ Basic hydroxide.	−	OH_2	=	K_2O Basic oxide or basic anhydride.
H_2SO_4 Acid.	−	OH_2 Water.	=	SO_3 Acid anhydride.
$Ca(HO)_2$ Basic hydroxide.	−	OH_2 Water.	=	CaO Basic oxide or basic anhydride.

The name *base* is still often given to compounds of this kind, but in view of the fact that this word is now universally applied to those compounds of nitrogen which combine with acids, it will save confusion if the word base is reserved for such nitrogenous compounds, while metallic oxides and hydroxides are merely qualified as *basic*. It must not be forgotten that when ammonia or a nitrogenous

base combines with an acid, a salt is alone formed without any secondary product; thus:



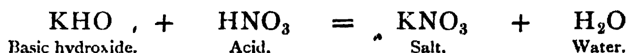
$$NH_3 + HNO_3 = NH_4NO_3$$

Ammonia. Nitric acid. Ammonium nitrate.

$$NH_2C_6H_5 + HC_2H_3O_2 = NH_3C_6H_5C_2H_3O_2$$

Aniline. Acetic acid. Aniline acetate.

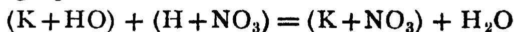
On the other hand, when a basic oxide or hydroxide interacts with an acid water is invariably formed in addition to the salt—



$$KHO + HNO_3 = KNO_3 + H_2O$$

Basic hydroxide. Acid. Salt. Water.

The demonstration of this fact is often neglected, but the formation of water is readily shown by bringing a stream of dry hydrogen chloride into a tube loosely filled with litharge and connected with a collecting tube kept cool. To represent a change of this kind according to modern views concerning the constitution of saline solutions, it is only necessary to write the formulæ of the acid, the basic hydroxide, and the salt in such a way as to indicate the constituent ions of each. Water is a compound which is but slightly, if at all, dissociated, and consequently the formula of the water produced represents a molecule. In the following equation



$$(K+HO) + (H+NO_3) = (K+NO_3) + H_2O$$

K and H are the positive ions and HO and NO_3 are the negative ions of caustic potash and nitric acid respectively. When they are mixed together the H and HO ions disappear from the field, having united together to form water molecules. In such an equation an explanation is provided of the fact to be mentioned later, that the heat generated by neutralising different acids by the same basic hydroxide is always about the same in amount. In such a process the heat produced does not proceed to any appreciable extent from the formation of the salt, but is due almost entirely to the formation of water. (See Chapter XIX.)

CHAPTER XV.

DERIVATIVES OF AMMONIA.

Ammonium Theory.—Ammonia is excessively soluble in water, and the solution has all the properties of a powerful alkali. Like caustic potash, it restores the blue colour to litmus which has been reddened by an acid, it absorbs carbonic acid from the air, it saturates acids, forming a class of crystallisable neutral salts, which are isomorphous with the corresponding salts of potassium. Like potash, also, it precipitates hydroxides when added to the solutions of a great many metallic salts, though in a few cases, *e.g.* with mercuric salts, it gives rise to compounds of a different character. Lastly, solution of ammonia differs from solution of caustic potash in that when evaporated it leaves no residue. In consequence of this want of stability, solution of ammonia is often referred to as the *volatile alkali*.

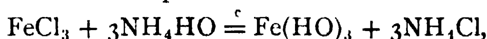
Guided by this marked resemblance between the compounds of ammonia and those of potassium, chemists have been led to regard both series as constituted in the same manner. Writing down in parallel columns a list of ammoniacal and potash salts, and eliminating from each pair of formulæ the symbols which are common to them both, we find that the group composed of one atom of nitrogen and four atoms of hydrogen, NH_4, is the residue left over in the one case, while the solitary symbol K remains in the other. The latter represents the radicle potassium, which, when isolated, presents all the characteristics of a metal.

The radicle *ammonium*, NH_4, has never been isolated, though it seems to be capable of a brief existence in the form of the remarkable substance known as ammonium amalgam. When a lump of sodium amalgam is placed in a solution of sal-ammoniac, or when the same salt, dissolved in water, is submitted to electrolysis, a globule of mercury

being used as the negative electrode, the mercury swells enormously, becoming so light as to float in the solution, and acquires a pasty consistence without losing its metallic aspect. In a few minutes the spongy mass contracts, hydrogen and ammonia escape, and the mercury recovers its original volume and lustre.

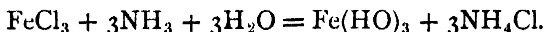
Compounds of			
	Ammonium.		Potassium.
$NH_3.H_2O$	or NH_4HO	or $AmHO'$	KHO
$NH_3.HCl$	or NH_4Cl	or $AmCl$	KCl
$NH_3.HNO_3$	or NH_4NO_3	or $AmNO_3$	KNO_3
$NH_3.H_2SO_4$	or NH_4HSO_4	or $AmHSO_4$	$KHSO_4$
$(NH_3)_2.H_2SO_4$	or $(NH_4)_2SO_4$	or Am_2SO_4	K_2SO_4
$NH_3H_3PO_4$	or $(NH_4)H_2PO_4$	or AmH_2PO_4	KH_2PO_4
$(NH_3)_2H_3PO_4$	or $(NH_4)_2HPO_4$	or Am_2HPO_4	K_2HPO_4
$(NH_3)_3H_3PO_4$	or $(NH_4)_3PO_4$	or Am_3PO_4	K_3PO_4

All the compounds of ammonium are characterised by the readiness with which they are dissociated into ammonia and an acid, and in solution of ammonia it appears that the amount of ammonium hydroxide actually present at any moment is very small, the greater part of it existing only potentially in the form of ammonia and water, which simultaneously act in the production of metallic hydroxides when the solution is mixed with solutions of metallic salts. When mixed with ferric chloride, for example, the greater part of the action is representable not as



$$FeCl_3 + 3NH_4HO = Fe(HO)_3 + 3NH_4Cl,$$

but by the following equation :—

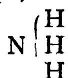


$$FeCl_3 + 3NH_3 + 3H_2O = Fe(HO)_3 + 3NH_4Cl.$$

Solution of ammonia constantly gives off ammonia gas recognisable by its pungency, which is also noticeable in the solid carbonate or smelling salts.

Amines.—The hydrogen of ammonia admits of substitution in three successive stages, and the compounds thus formed are believed to be constituted in the same manner

as ammonia itself, or, using the ordinary expression, they belong to the ammonia type,



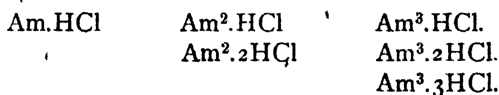
$$N\begin{cases}H\\H\\H\end{cases}$$

the replacing radicles being severally combined with the nitrogen in the same manner as the hydrogen atoms of the type.

When positive radicles, consisting of metals or hydrocarbons, are substituted for the hydrogen in the ammonia molecule, the resulting compounds retain the alkalinity and general basic character of ammonia. Such compounds are called *amines*. They generally combine with acids, but are unaffected by treatment with alkalies. There are several classes of amines resulting from the more or less extensive replacement of the hydrogen or the coalescence of two or more molecules of ammonia. Their constitution will be understood after inspection of the following table, in which the symbol R represents a positive radicle, the valency of which is indicated by dashes :—

Monamines.	Diamines.	Triamines.
Primary. $N\begin{cases}R'\\H\\H\end{cases}$	Primary. $N_2\begin{cases}R''\\H_2\\H_2\end{cases}$	Primary. $N_3\begin{cases}R'''\\H_3\\H_3\end{cases}$
Secondary. $N\begin{cases}R'\\R'\\H\end{cases}$	Secondary. $N_2\begin{cases}R''\\R''\\H_2\end{cases}$ $N_2\begin{cases}R''\\R'_2\\H_2\end{cases}$	Secondary. $N_3\begin{cases}R'''\\R'''\\H_3\end{cases}$ $N_3\begin{cases}R'''\\R'_3\\H_3\end{cases}$ &c.
Tertiary. $N\begin{cases}R'\\R'\\R'\end{cases}$	Tertiary. $N^2\begin{cases}R''\\R''\\R''\end{cases}$ $N_2\begin{cases}R''\\R''\\R'_2\end{cases}$ $N_2\begin{cases}R''\\R'_2\\R'_2\end{cases}$	Tertiary. $N_3\begin{cases}R'''\\R'''\\R'''\end{cases}$ $N_3\begin{cases}R'''\\R'''\\R'_3\end{cases}$ $N_3\begin{cases}R'''\\R'_3\\R'_3\end{cases}$ &c.

Monamines are capable of saturating only one molecule of a monobasic acid, but diamines unite with two, and triamines with three molecules of such acids. The diamines and triamines also yield intermediate compounds. Representing the monamines, diamines, and triamines respectively by the symbols Am, Am^2, and Am^3, the general formulæ of the chlorides may be written in the following manner:

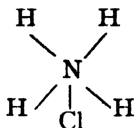


Am.HCl	Am^2.HCl	Am^3.HCl.
	Am^2.2HCl	Am^3.2HCl.
		Am^3.3HCl.

The tertiary amines unite with iodides and other salts of alcohol radicles in the same manner as with acids, furnishing compounds which may be formulated either as ammonia compounds or as derived from the hypothetical ammonium radicle. Thus triethyl-amine combines with ethyl iodide, forming a crystalline compound, which may be represented either as $N(C_2H_5)_3.C_2H_5I$, or, more consistently and conveniently, as tetrethyl-ammonium iodide $N(C_2H_5)_4I$. This compound is obviously the analogue of ammonium iodide. When acted upon by silver oxide and water, it exchanges iodine for hydroxyl, and gives rise to a hydroxide of tetrethyl-ammonium, $N(C_2H_5)_4HO$, a compound which may be obtained in the solid state, and which in its causticity and alkalinity closely resembles potassium hydroxide. The existence of this compound, and others of similar nature, furnishes strong evidence in favour of the ammonium theory. Like their hypothetical prototype the substituted ammonium radicles $N(C_2H_5)_4$, &c. are not known in the free state.

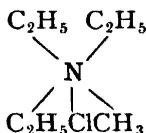
Another question has at different times been raised regarding the constitution of ammonium compounds. It is now generally admitted that they contain pentad nitrogen,

ammonium chloride being represented graphically by the formula—



and other ammonium compounds in a corresponding manner. Experiment has been brought to bear on the subject in the following manner :

Methyl-triethyl ammonium chloride may be represented either as an ammonium compound—



or, as formed on the type of sal-ammoniac, regarded as ammonia hydrochloride, $NH_3.HCl$. If the latter view were correct, there ought to be two isomeric compounds having the formulæ—

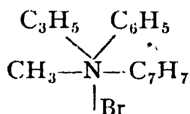


$$N(C_2H_5)_3.CH_3Cl \text{ and } N(C_2H_5)_2(CH_3).C_2H_5Cl.$$

It is found, however, that the result of bringing together triethylamine and methyl chloride, is a body identical in every respect with the product obtained by combining methyl-diethylamine with ethyl chloride.

According to the ammonium formula, which these results support, each radicle is in the same position with respect to the nitrogen, and no isomerism is possible so long as the atoms are represented as lying in the same plane. Quite recently it has been found that when combined with five different radicles nitrogen is capable of exhibiting the same kind of isomerism which has been described in connection with the compounds of carbon, and

which is explained by assuming that the arrangement of the substituting radicles in space is such as to give rise to asymmetry in the compound (see pp. 104 and 125). The salts of benzylphenylallylmethylammonium, for example, have been obtained in two forms, which undoubtedly contain five radicles combined with the atom of pentad nitrogen—



and which bear towards each other the same kind of relation which has so long been known in tartaric acid and other compounds in which the central element is a carbon atom. These pairs of nitrogen compounds present, the one a dextrorotatory power, the other a corresponding lævo-rotatory power, and their constitution is believed to be respectively that of an object and its image in a mirror.

Phosphines, Arsines, Stibines.—By replacing the hydrogen of phosphoretted, arsenetted, and antimonetted hydrogen by hydrocarbon groups, extensive series of bases are obtained, which have received the above names, and, save for their extreme oxidability, and in many cases incapacity for combination with acids, agree in general characters with the compound ammonias.

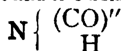
Amides.—When the hydrogen of ammonia is replaced by oxidised or other negative radicles, compounds called *amides* are formed. These substances are, generally speaking, neutral, though some which contain the radicles of weak acids are still capable of entering into combination with acids, and a few are even very decidedly basic; urea or carbamide, $CO\ (NH_2)_2$, for example.

On the other hand, some of the amides derived from polybasic acids are themselves acid bodies. This has been already referred to (Acids, p. 246).

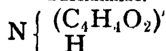
The general formulæ of amides correspond with those of

amines, and they may be classified into primary, secondary and tertiary monamides, diamides, and triamides, and, substituting negative R or $\overline{R}$ for R in the formulæ given on p. 253, they may be tabulated in the same way as the amines. One slight addition is necessary. Monamines containing bivalent radicles are not known, but monamides in which two atoms of hydrogen are replaced by one bivalent acid radicle, are known under the name imides.

Cyanic acid or Carbimide.



Succinimide.

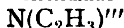


Tertiary derivatives of ammonia, called nitriles or cyanides (p. 119), are known in which the three atoms of hydrogen are replaced by trivalent hydrocarbon groups. We have, for example,

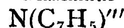
Formonitrile



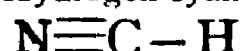
Acetonitrile



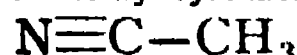
Benzonitrile



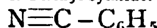
or Hydrogen cyanide.



or Methyl cyanide.

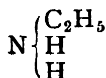


or Phenyl cyanide.

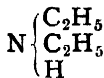


These compounds are not basic, and are decomposed, like all amides, by boiling with alkalis. Ammonia is evolved, and a salt formed corresponding with the acid from the ammonium salt of which they are derived by dehydration. Notwithstanding, therefore, that the replacing radicle contains no oxygen, these compounds should be ranked with the amides. The isocyanides (p. 120) are basic, and are therefore called carb*amines*.

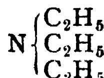
The residual hydrogen of primary and secondary amides may be replaced by positive or hydrocarbon radicles. Compounds intermediate between amines and amides then result. The following are examples :—



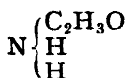
Ethylamine

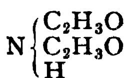


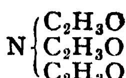
Diethylamine.

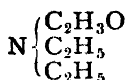


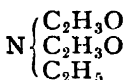
Triethylamine.

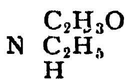

Acetamide.


Diacetamide.


Triacetamide.


Diethylacetamide.


Ethyldiacetamide.


Ethylacetamide.

CHAPTER XVI.

CARBON COMPOUNDS.

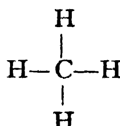
COMPOUNDS having the same chemical functions, and constituting a series in which, between any two contiguous terms, there is a constant difference of CH_2, are said to be homologous, and the series is a *homologous series.* Relations of a like nature have not hitherto been observed among the compounds of any element but carbon.[1] This peculiarity seems to be connected with a special faculty with which carbon atoms appear to be endowed, the power, namely, of uniting with one another without the intervention of any other element. Thus a very large number of different compounds containing carbon and hydrogen, either alone or associated with oxygen or nitrogen, have already been produced, and a still larger number of possible combinations of carbon is indicated by theory.

By reason of their composition being unknown or their reactions imperfectly studied, many carbon compounds remain unclassified, but the number of these has been greatly reduced by modern researches. The following are the most important classes of carbon compounds :—

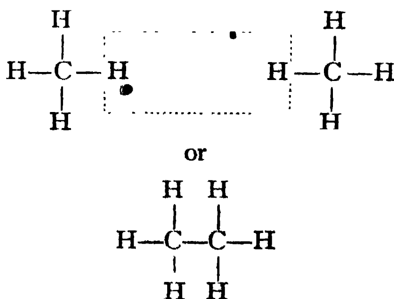
[1] And probably silicon.

I. HYDROCARBONS AND THEIR HALOID DERIVATIVES.

Some hundreds of compounds consisting only of carbon and hydrogen have been described, but no such compound is known of which two volumes of the vapour contain a larger quantity of hydrogen than is represented by the general formula C_nH_{2n+2}. The fact is explained by the following hypothesis. A single atom of carbon has four units of combining capacity, each of which is capable of being saturated by one atom of hydrogen. We thus arrive at the formula



which represents marsh gas. This compound is absolutely saturated, and nothing will induce it to take up additional elements of any kind, except on condition of removing one or more of its hydrogen atoms. If, now, we imagine another atom of carbon similarly loaded with hydrogen presented to it, the only mode in which they can unite together is by the severance of an atom of hydrogen from each group, as represented in the following diagram :—



The same process may be repeated *ad infinitum*. The number of hydrogen atoms in the first term of the series being 4, in the second $2 \times 4 - 2$, in the third $3 \times 4 - 4$, in the n^{th} term the number will be $4n - (2n - 2)$, or $2n + 2$.

The most important series of hydrocarbons at present known are represented by the following general formulæ :—

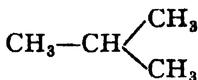
Paraffins, or Marsh Gas Series,	C_nH_{2n+2}
Olefines, or Olefiant Gas Series,	C_nH_{2n}
Acetylene Series,	C_nH_{2n-2}
Terpene Series,	C_nH_{2n-4}
Benzene Series,	C_nH_{2n-6}
Naphthalene Series,	C_nH_{2n-12}
Anthracene Series,	C_nH_{2n-18}.

From what has already been said as to the manner in which the carbon atoms in a carbon compound become linked together, it is obvious that these general formulæ admit of development in a variety of ways, so as to give rise in each series to a considerable number of isomerides. Thus, if we take the formula for the paraffins, and assign different values to *n* we arrive at such results as the following :—

CH_4	$n = 1$
$CH_3—CH_3$	$n = 2$
$CH_3—CH_2—CH_3$	$n = 3$
$CH_3—CH_2—CH_2—CH_3$	$n = 4$
&c.	&c.

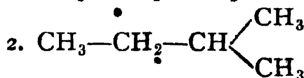
Now it is obvious that in the first, second, and third terms of such a series, on the assumption that H is always monad and C tetrad, there cannot be any other arrangement of the symbols. In other words, there can only be one compound of the formula CH_4, one C_2H_6, and one C_3H_8. Isomerism is impossible. But on arrival at the fourth member

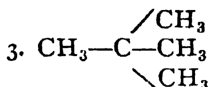
of the series, C_4H_{10}, we find it possible to arrange the symbols in a second order as follows :—



The fifth term admits of a still larger number of varieties, which may be expressed in a similar manner.







As we advance in the series the number of isomeric hydrocarbons theoretically possible increases very rapidly, and it has been calculated that at the tenth term, $C_{10}H_{22}$, there may be 75 modifications, whilst at the thirteenth, $C_{13}H_{28}$, there may be no fewer than 799 varieties of formula. The number of these hydrocarbons actually known is at present very small.

In the formula for the olefines and for the acetylene series we must admit the supposition that the carbon atoms are linked together by more than one unit of valency.



The terpenes are liquid hydrocarbons found in turpentine and in various natural essential oils. They all have the formula $C_{10}H_{16}$, and no homologues have yet been discovered. Their constitution is at present unknown.

On reviewing the foregoing formulæ it will at once be perceived that while the paraffins are saturated,[1] and hence

[1] The paraffins are more completely saturated than any other known form of matter, for not only do they resist the attack of ordinary chemical agents but they form no 'molecular' combinations, and even as solvents the liquid members of the series have but limited application.

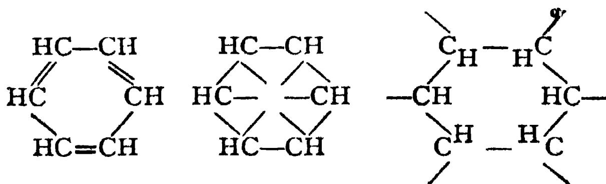
are capable of producing only substitution compounds, the remaining series referred to may enter into direct combination with hydrogen, with the halogens, and other substances. Thus the following formulæ represents saturated compounds :—



Olefines	$C_nH_{2n}Br_2$
Acetylene series	$C_nH_{2n-2}Br_4$.

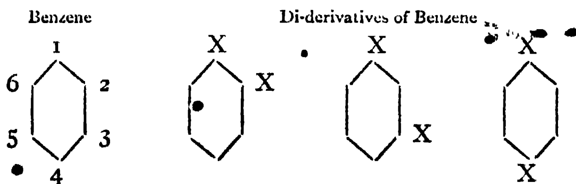
If now we recall the hypothesis already explained (pp. 104 and 124) which is employed to account for optical activity in carbon compounds, it can easily be shown with the aid of models, or even carefully drawn diagrams, that when a number of atoms of carbon are joined together the chain which is produced cannot lie in a straight line as apparently indicated by the usual symbolic formulæ. A series of three or more carbon atoms must form a spiral, one turn of which is produced by a number just over five and less than six such atoms. A closed ring may therefore be formed most easily by five or six atoms of carbon, because the fifth atom, or the sixth, comes very near to the first atom of the chain, and if other conditions are favourable the spiral will resolve itself into a series of closed rings. As a matter of fact, it is found that compounds in which there is reason to believe that five or six atoms of carbon are thus united together are very stable and exhibit characteristic reactions, in all of which the cluster or ring remains unbroken. In some cases one or more of the carbon atoms in such a ring is replaced by an atom of nitrogen or of sulphur or of oxygen.

The constitution of benzene, for example, may be represented by one of the following formulæ :—



It is an open question whether the atoms of carbon are united together by alternate single and double links or whether they all influence one another in some unexplained manner as in the second, usually called the 'centric,' formula, or whether the fourth unit of valency is simply unoccupied as indicated in the third formula.

These formulæ agree in representing the carbon as forming a closed chain, and all account for the following facts. (1) Benzene is the first term of the series, there being no hydrocarbon homologous with benzene containing fewer than six atoms of carbon. (2) Benzene is capable of combining with six atoms of bromine and no more. (3) Benzene gives rise to a large number of substitution derivatives, but of those in which one hydrogen atom is replaced by one monad atom or group there can be no isomerides, because all the six atoms of hydrogen are similarly situated. Of those substitution derivatives in which two atoms of hydrogen are replaced by two monads there are three isomeric modifications. To explain this we number the points of the hexagon at which the carbon symbols are placed, and omitting for the sake of clearness all but the symbols of the replacing radicles, we see at once in what manner these three modifications of the di-derivatives are related to the original hydrocarbon and to one another.



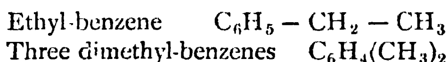
The symbol X represents Cl, Br, I, NO_2, NH_2, CH_3, or other monad radicle. In the first of these formulæ the replacing symbols are represented in the positions 1 and 2, in the second 1 and 3, and in the third 1 and 4. It must,

however, be observed that the symbols of carbon to which they are attached are all of the same kind, and it therefore matters not which of these carbons is used as the starting point and in which direction the numbering is carried. The first formula, therefore, merely indicates that the replacing radicles are combined with two contiguous atoms of hydrogen, whilst the second and third formulæ represent them as more widely separated.

In each case the same structure is implied so long as the relative distances from each other of the symbols of X are preserved upon the chain of carbon.

The modifications of the tri and tetra-substitution derivatives of benzene are accounted for by the same hypothesis.

The higher homologues of benzene result from the introduction of the methyl group, CH_3, in place of one or more atoms of hydrogen. Monomethyl benzene, commonly called toluene, $C_6H_5(CH_3)$, cannot exist in more than one form, as already explained. But the next term of the series, xylene, may exhibit no fewer than four isomeric modifications, as follows:—

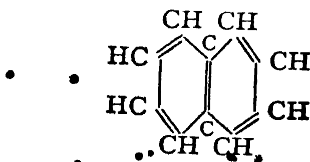

Ethyl-benzene $C_6H_5 - CH_2 - CH_3$
Three dimethyl-benzenes $C_6H_4(CH_3)_2$

	Position of methyl.
First modification	1 : 2
Second ,,	1 : 3
Third ,,	1 : 4

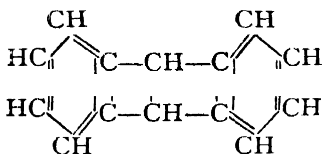
The number of modifications is still greater among the higher members of the series.

The constitution of the hydrocarbons naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, and their homologues is regarded as closely related to that of benzene, naphthalene being

represented as composed of a pair of benzene molecules possessing two atoms of carbon in common :—



In anthracene two molecules of benzene are connected together by a link composed of two additional atoms of carbon, thus :—



These formulæ indicate that the number of isomeric derivatives of naphthalene and of anthracene must be much larger than in the case of benzene. Many of these have already been isolated and their properties determined. They include a number of important dye-stuffs.

Hydrocarbons differ very much in their physical properties, and in the nature of the reactions to which they lend themselves. This, of course, depends upon the series to which they belong ; but taking any one series, such as the paraffins, it is found that a regular gradation may be traced in the physical properties of the several members of the series, passing from the lowest to the highest terms.

Thus the first three members of the paraffin series are gaseous ; the succeeding members are liquid, but become less and less volatile, and at the same time more dense and viscid, till among the highest members of the series we come to crystalline solid bodies, which are volatilisable only at such high temperatures that they cannot be distilled without extensive decomposition. In proportion as we

ascend the series the percentage of hydrogen rapidly decreases, and this, together with the diminished mobility of the body, may perhaps account for the comparative indifference to chemical reagents exhibited by the higher members.

Paraffins.

		Molecular Weight.	Boiling Point
Methane	CH_4 . . .	16	gaseous
Ethane	C_2H_6 . .	30	gaseous
Propane	C_3H_8 . .	44	gaseous
Tetrane	C_4H_{10} . .	58	1°
Pentane	C_5H_{12} . .	72	38°
Hexane	C_6H_{14} . .	86	70°
Heptane	C_7H_{16} . .	100	99°
Octane	C_8H_{18} . .	114	124°
	C_nH_{2n+2}	&c.	&c

In this series, for every increase of 14 on the molecular weight, the boiling point rises by about 30° to 35°.

A corresponding seriation of properties, both physical and chemical, is observed in other homologous series.

2. ALCOHOLS.

These compounds may be regarded as hydroxides of hydrocarbon radicles, considering that in their most prominent and characteristic reactions they resemble water and the hydroxides of the metals. They are either liquids or solids, and they are obtained in a variety of processes; but the ethylic or common alcohol of fermentation was the first studied, and is the best known of the class. Taking it as the representative of alcohols in general, we may record the following as its characteristic reactions:—

(*a*) By the action of an alkali metal it loses hydrogen.



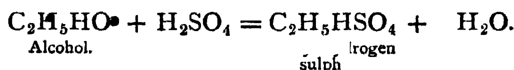
$$C_2H_5HO + K = C_2H_5KO + H.$$

Alcohol. Potassium ethylate.

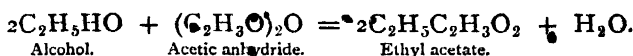
(*b*) By the action of acids or acid anhydrides it is converted into salts, called compound ethers, or *esters*, *e.g.* :



$$\underset{\text{Alcohol.}}{C_2H_5HO} + HCl = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + H_2O.$$



$$\underset{\text{Alcohol.}}{C_2H_5HO} + H_2SO_4 = \underset{\text{...rogen sulph...}}{C_2H_5HSO_4} + H_2O.$$



$$\underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Acetic anhydride.}}{(C_2H_3O)_2O} = \underset{\text{Ethyl acetate.}}{2C_2H_5C_2H_3O_2} + H_2O.$$

(*c*) The alcohol is reproduced from these salts by the action of alkalies :



$$C_2H_5Cl + KHO = C_2H_5HO + KCl.$$

Alcohols are divisible into several classes, according to the number of hydroxyl groups in the molecule. Monohydric alcohols yield one saline derivative or ester, dihydric alcohols give two, trihydric alcohols give three such compounds, and so on.

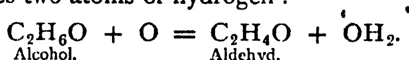
The following formulæ, which represent three typical alcohols and the chlorides derivable from them, will serve to illustrate this statement.

Common alcohol. Monohydric.	Glycol. Dihydric.	Glycerol. Trihydric.
C_2H_5HO	$C_2H_4\begin{cases}HO\\HO\end{cases}$	$C_3H_5\begin{cases}HO\\HO\\HO\end{cases}$
		$C_3H_5\begin{cases}HO\\HO\\Cl\end{cases}$
	$C_2H_4\begin{cases}HO\\Cl\end{cases}$	$C_3H_5\begin{cases}HO\\Cl\\Cl\end{cases}$
C_2H_5Cl	$C_2H_4\begin{cases}Cl\\Cl\end{cases}$	$C_3H_5\begin{cases}Cl\\Cl\\Cl\end{cases}$

But alcohols are also divisible into several other groups,

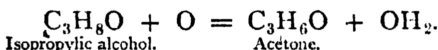
which are characterised by their behaviour when submitted to oxidation.

Primary alcohols, when oxidised, lose hydrogen, and yield compounds which are called aldehyds ; thus common alcohol loses two atoms of hydrogen :



$$\underset{\text{Alcohol.}}{C_2H_6O} + O = \underset{\text{Aldehyd.}}{C_2H_4O} + OH_2.$$

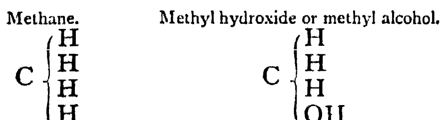
Secondary alcohols, under the influence of similar reagents, yield ketones ; for example :



$$\underset{\text{Isopropylic alcohol.}}{C_3H_8O} + O = \underset{\text{Acetone.}}{C_3H_6O} + OH_2.$$

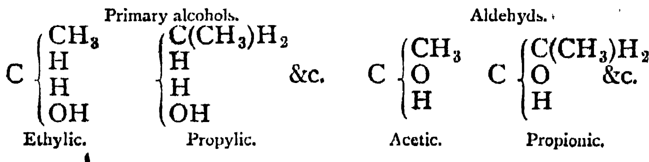
Tertiary alcohols, when oxidised, break up into a mixture of acids, each containing a smaller number of carbon atoms than the alcohol.

These differences are accounted for by the following hypothesis. The generating hydrocarbon is supposed to be marsh-gas or methane, and by the replacement of one of its hydrogen atoms by hydroxyl, an alcohol called methylic alcohol is formed.



$$\underset{\text{Methane.}}{C\begin{cases}H\\H\\H\\H\end{cases}} \qquad \underset{\text{Methyl hydroxide or methyl alcohol.}}{C\begin{cases}H\\H\\H\\OH\end{cases}}$$

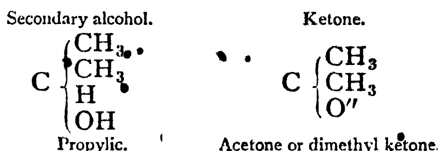
By replacing another atom of hydrogen by a hydrocarbon group, one of the higher homologues of methyl alcohol is produced. Now, so long as the replacement is effected in such a manner as to leave two of the hydrogen atoms of the marsh-gas type undisturbed, the product is a primary alcohol, which by the substitution of an atom of oxygen for these two atoms of hydrogen is capable of giving rise to an aldehyd.



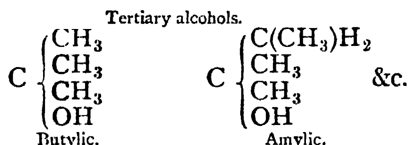
Primary alcohols. — Aldehyds.

$$\underset{\text{Ethylic.}}{C\begin{cases}CH_3\\H\\H\\OH\end{cases}} \quad \underset{\text{Propylic.}}{\begin{cases}C(CH_3)H_2\\H\\H\\OH\end{cases}} \ \&c. \qquad \underset{\text{Acetic.}}{C\begin{cases}CH_3\\O\\H\end{cases}} \quad \underset{\text{Propionic.}}{C\begin{cases}C(CH_3)H_2\\O\\H\end{cases}} \ \&c.$$

If, however, the second step in the process of replacement affects one of these typical hydrogen atoms, then a secondary alcohol is produced, and this compound cannot take in oxygen in the same manner as the primary alcohols, but it may lose two atoms of hydrogen, as represented by the following formula:



Lastly, the tertiary alcohols are generated in the same manner by the replacement of the last atom of hydrogen originally belonging to the type, thus:



It is obvious from this that, although a primary alcohol may contain one or two atoms of carbon, no secondary alcohol containing less than three atoms, and no tertiary alcohol containing less than four atoms of carbon in the molecule can exist.

Another class of alcohols, called phenols, is also known. These agree to some extent with secondary alcohols, inasmuch as they yield no aldehyd by oxidation, but furnish compounds containing the same number of carbon atoms as themselves. These substances, however, are not ketones. They are called quinones.

No phenol is known to contain fewer than six carbon atoms in the molecule. They are regarded as derived from benzene or some analogous hydrocarbon. The best known phenol is the compound which usually goes by that name among chemists, or, in common parlance, carbolic acid,

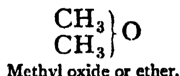
C_6H_5OH. In accordance with the formula, it might also be called phenyl hydroxide, or phenyl alcohol. It differs from ordinary alcohols in yielding a great number of substitution derivatives, most of which exhibit well-marked acid properties. Thus the trinitrophenol is commonly called picric, or trinitrophenic acid. The following are the formulæ of its chloro- and nitro derivatives:

Monochlorophenol .	$C_6H_4Cl.OH$
Dichlorophenol .	$C_6H_3Cl_2.OH$
Trichlorophenol .	$C_6H_2Cl_3.OH$
Pentachlorophenol .	$C_6Cl_5.OH$
Mononitrophenol .	$C_6H_4(NO_2).OH$
Dinitrophenol .	$C_6H_3(NO_2)_2.OH$
Trinitrophenol .	$C_6H_2(NO_2)_3.OH$

Several isomeric modifications of the mono- and di-derivatives are known.

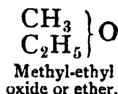
3. ETHERS.

These compounds have the same relation to alcohols as the metallic oxides to their hydroxides. They are, however, not easily converted into alcohols by the direct action of water, neither are they obtained from alcohols so readily as the metallic oxides from hydrates. The oxides corresponding with the dihydric alcohols seem to undergo this transformation more readily than those belonging to the monohydric alcohols. The following are some examples of simple and mixed ethers:



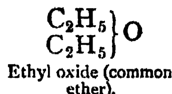
$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$

Methyl oxide or ether.



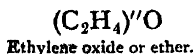
$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$

Methyl-ethyl oxide or ether.



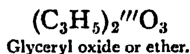
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$

Ethyl oxide (common ether).



$(C_2H_4)''O$

Ethylene oxide or ether.



$(C_3H_5)_2'''O_3$

Glyceryl oxide or ether.

The known ethers are volatile liquids of aromatic odour.

4. ALDEHYDS AND KETONES.

These two classes of compounds are closely related, both as regards their mode of formation, and properties and composition.

Aldehyds are formed by the oxidation of primary alcohols, ketones by the oxidation of secondary alcohols. Thus common aldehyd results from the removal of two atoms of hydrogen from common (ethyl) alcohol :—



$$C_2H_6O \quad - \quad H_2 \quad = \quad C_2H_4O.$$

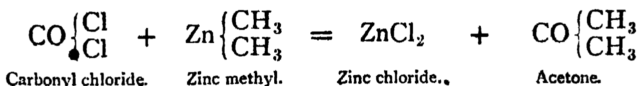
Acetone, the best known of the ketones, stands in the same relation towards isopropylic alcohol :—



$$C_3H_8O \quad - \quad H_2 \quad = \quad C_3H_6O.$$

It has already been shown that no secondary alcohol can contain less than three atoms of carbon, and consequently there can be no ketone, properly so called, containing less carbon than acetone, C_3H_6O.

The formation of this compound by the action of zinc methyl (see *organo-metallic compounds*) on carbonyl chloride shows that it contains two methyl groups united with the carbonyl radicle :—

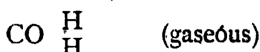


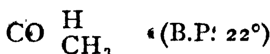
$$CO\begin{cases}Cl\\Cl\end{cases} + Zn\begin{cases}CH_3\\CH_3\end{cases} = ZnCl_2 + CO\begin{cases}CH_3\\CH_3\end{cases}$$

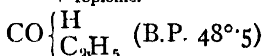
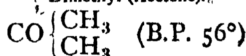
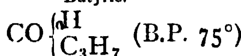
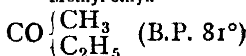
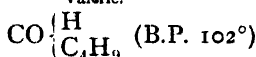
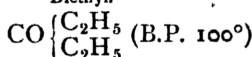
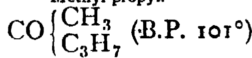
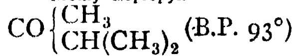
Carbonyl chloride. Zinc methyl. Zinc chloride. Acetone.

It thus appears that the aldehyds of the monocarbon and dicarbon series may be considered to be homologous with the higher aldehyds on the one hand, and with the ketones on

the other. The following formulæ indicate the relationship:—

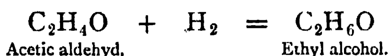
Formic aldehyd or ketone.  $CO\begin{matrix}H\\H\end{matrix}$ (gaseous)

Acetic aldehyd or ketone.  $CO\begin{matrix}H\\CH_3\end{matrix}$ (B.P. 22°)

Aldehyds.	Ketones.
Propionic.  $CO\begin{cases}H\\C_2H_5\end{cases}$ (B.P. 48°·5)	Dimethyl (Acetone).  $CO\begin{cases}CH_3\\CH_3\end{cases}$ (B.P. 56°)
Butyric.  $CO\begin{cases}H\\C_3H_7\end{cases}$ (B.P. 75°)	Methyl-ethyl.  $CO\begin{cases}CH_3\\C_2H_5\end{cases}$ (B.P. 81°)
Valeric.  $CO\begin{cases}H\\C_4H_9\end{cases}$ (B.P. 102°)	Metameric. Diethyl.  $CO\begin{cases}C_2H_5\\C_2H_5\end{cases}$ (B.P. 100°)
	Metameric. Methyl-propyl.  $CO\begin{cases}CH_3\\C_3H_7\end{cases}$ (B.P. 101°)
	Metameric. Methyl-isopropyl.  $CO\begin{cases}CH_3\\CH(CH_3)_2\end{cases}$ (B.P. 93°)

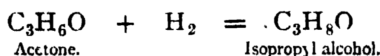
From the existence of such intimate relations between these two classes of compounds it is not extraordinary that in many of their properties there should be considerable resemblance between them.

(a) By the action of nascent hydrogen, generated by the action of sodium amalgam in the presence of water, aldehyds and ketones are converted into the corresponding alcohols, *e.g.* :—



$$C_2H_4O + H_2 = C_2H_6O$$

Acetic aldehyd. — Ethyl alcohol.



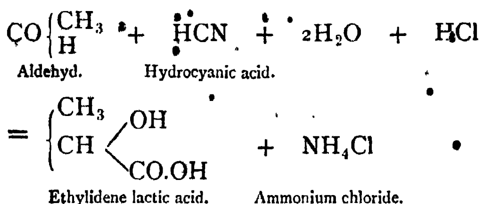
$$C_3H_6O + H_2 = C_3H_8O$$

Acetone. — Isopropyl alcohol.

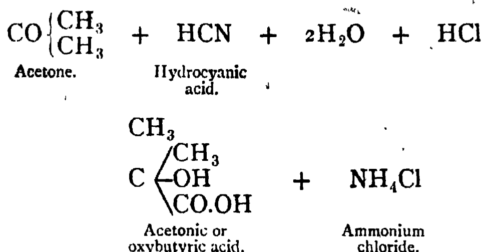
(*b*) All aldehyds and many ketones combine with the acid sulphite of sodium, forming crystallisable compounds,

which yield up the aldehyd or ketone again by treatment with an acid or an alkaline carbonate.

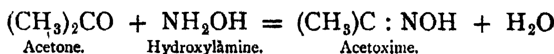
(*c*) By boiling with hydrocyanic acid and hydrochloric acid, aldehyds and ketones are converted into acids containing in the molecule one more atom of carbon than themselves. For example, common aldehyd is converted into one form of lactic acid:



Acetone is converted by a similar process into a homologue of lactic acid:

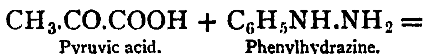


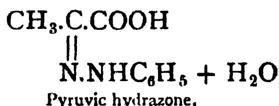
(*d*) Aldehyds and ketones in aqueous solution interact readily with hydroxylamine, giving rise to compounds which contain the residue $=N.OH$ in place of oxygen. These were originally called hydroximides, but are now generally known as *oximes*, and are divisible into the two classes of aldoximes and ketoximes according to their constitution. Their formation may be illustrated by one example:



The oximes are usually decomposed by boiling with acids, hydroxylamine and the aldehyd or ketone being regenerated.

(*e*) Aldehyds and ketones also interact in a somewhat similar manner with phenylhydrazine, $C_6H_5NH.NH_2$, water being eliminated. The products are called hydrazones. The reaction occurs even when the molecule of the aldehyd or ketone has been partly altered, provided the carbonyl group CO remains. Thus, pyruvic acid, $CH_3.CO.COOH$, may be regarded as acetone in which one methyl group has been oxidised. It reacts with phenylhydrazine in the normal manner thus :—





So that hydroxylamine and phenylhydrazine are reagents which are usefully employed for recognising the presence of the characteristic ketonic group in such compounds, and determining the number of such groups if more than one are present. Compounds called osazones are formed by the action of excess of phenylhydrazine in the presence of air or oxidising agents upon the more complex aldehyds and ketones.

Notwithstanding these various points of resemblance, ketones are sharply distinguished from aldehyds by the action of agents of oxidation.

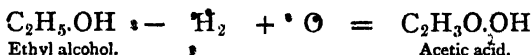
An aldehyd is always converted by oxidation into an acid containing the same number of atoms of carbon.

A ketone, on the contrary, is much more difficult to oxidise, and is then broken up into a mixture of acids, each containing a smaller number of carbon atoms. This oxidation proceeds according to a definite law.

5. ACIDS.

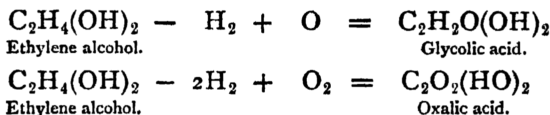
Every carbon acid may be considered to have been derived from an alcohol by the substitution of an atom of oxygen for two atoms of hydrogen.

Monohydric alcohols yield monobasic acids. For example, ethylic alcohol yields acetic acid :



$$\underset{\text{Ethyl alcohol.}}{C_2H_5.OH} - H_2 + O = \underset{\text{Acetic acid.}}{C_2H_3O.OH}$$

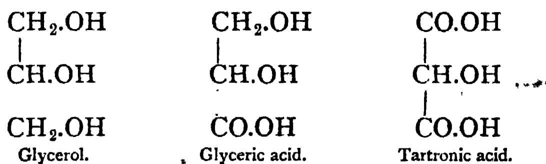
Dihydric alcohols may yield either monobasic or dibasic acids. Ethylene alcohol or glycol, for example, may be converted into monobasic glycolic or dibasic oxalic acid, thus :



$$\underset{\text{Ethylene alcohol.}}{C_2H_4(OH)_2} - H_2 + O = \underset{\text{Glycolic acid.}}{C_2H_2O(OH)_2}$$

$$\underset{\text{Ethylene alcohol.}}{C_2H_4(OH)_2} - 2H_2 + O_2 = \underset{\text{Oxalic acid.}}{C_2O_2(HO)_2}$$

Trihydric alcohols may yield theoretically either monobasic, dibasic, or tribasic acids. Very few of these derivatives, however, are actually known. Glycerol, a trihydric alcohol, yields, upon oxidation, monobasic glyceric acid and dibasic tartronic acid :



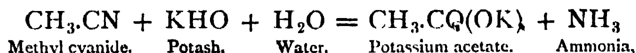
Glycerol.	Glyceric acid.	Tartronic acid.
$CH_2.OH$	$CH_2.OH$	$CO.OH$
$CH.OH$	$CH.OH$	$CH.OH$
$CH_2.OH$	$CO.OH$	$CO.OH$

A large number of acids are known, the alcohols corresponding to which have not yet been discovered.

Acids, however, may be generated by an entirely different process from alcohols containing one atom less carbon. This process is interesting, because it serves to indicate the general constitution of carbon acids.

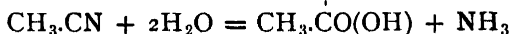
Starting from methyl alcohol, $CH_3.OH$, for example, we

may convert it into the corresponding cyanide, $CH_3.CN$. When boiled with caustic potash this compound undergoes decomposition, ammonia is evolved, and the potassium salt of acetic acid is generated :



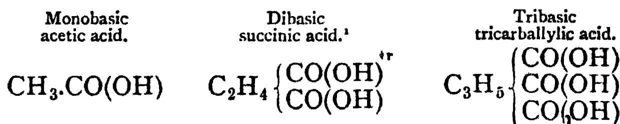
$$\underset{\text{Methyl cyanide.}}{CH_3.CN} + \underset{\text{Potash.}}{KHO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium acetate.}}{CH_3.CO(OK)} + \underset{\text{Ammonia.}}{NH_3}$$

Or, leaving the potassium out of sight, the reaction may be represented as follows :



$$CH_3.CN + 2H_2O = CH_3.CO(OH) + NH_3$$

From this it appears that the acid is generated by the substitution of $O'' + (OH)'$ for the N''' of the cyanide. Acetic acid, then, consists of a methyl group, CH_3, combined with a *carboxyl* group, CO.OH. Now methyl alcohol is monohydric, and therefore is capable of yielding one cyanide and no more. Consequently, from methyl alcohol only one derivative containing the carboxyl group can be formed, and that derivative is a monobasic acid. In a similar manner it is found that, by decomposing the cyanide of a bivalent alcohol radicle by boiling alkali, a bibasic acid is produced, whilst the cyanide of a trivalent radicle yields by the same process a tribasic acid. Setting down examples of compounds generated in this way, we find that they all contain the group CO.OH, once, twice, or three times in the molecule, according to the saturating power of the acid.



Monobasic acetic acid.	Dibasic succinic acid.[1]	Tribasic tricarballylic acid.
$CH_3.CO(OH)$	$C_2H_4\begin{cases}CO(OH)\\CO(OH)\end{cases}$	$C_3H_5\begin{cases}CO(OH)\\CO(OH)\\CO(OH)\end{cases}$

This carboxyl group, then, is contained in a very large number of carbon acids, and its presence seems to be intimately connected with the development of the acid

[1] See Molecular Weight, Chap. VI. p. 92

character in these compounds. We have seen (Phenols, p. 269) that the halogens and the nitroxyl group $(NO_2)'$, when substituted for hydrogen in certain oxidised bodies, also constitute acidifying agents, but the presence of these radicles in varying quantities does not affect the basicity of the resulting acid; whereas it seems to have been established that an acid which contains the carboxyl, CO(OH), group *n* times is *n* basic.

Carbon acids, when submitted to the action of the halogens, yield a great many substitution derivatives, such as the following chlorinated compounds, which are obtained from acetic acid :—

Monochloracetic acid	$CH_2Cl.COOH$
Dichloracetic acid	$CHCl_2.COOH$
Trichloracetic acid	$CCl_3.COOH$

But here the process of substitution stops, the hydrogen of the carboxyl being replaceable only by metallic or positive radicles, and not by negative bodies.

The metallic salts, amides, anhydrides, and chlorides derived from a carbon acid, correspond in number, mode of formation, and general properties with the same derivatives of mineral acids (pp. 242 to 248).

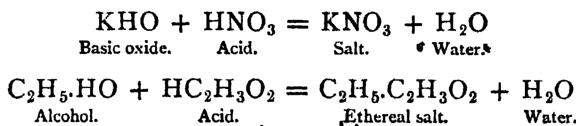
6. BASIC DERIVATIVES OF AMMONIA.

The constitution and general properties of these compounds have already been discussed (Amines, p. 252).

7. COMPOUND ETHERS OR ESTERS.

The most general method for the formation of these compounds consists in heating together an acid and an alcohol. A double decomposition ensues; water is formed, together with the ester; so that the reaction is exactly

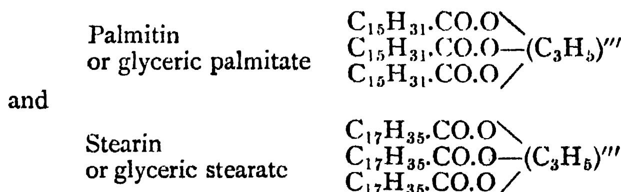
parallel with the change which occurs when an ordinary acid and basic oxide are brought into contact. The following equations, for example, are strictly comparable :—



$$\underset{\text{Basic oxide.}}{KHO} + \underset{\text{Acid.}}{HNO_3} = \underset{\text{Salt.}}{KNO_3} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Alcohol.}}{C_2H_5.HO} + \underset{\text{Acid.}}{HC_2H_3O_2} = \underset{\text{Ethereal salt.}}{C_2H_5.C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

Esters also imitate metallic salts in their general reactions. Thus they are decomposed by acids, by alkalies, and by water in precisely the same manner, though usually more slowly. They differ from metallic salts, however, in many physical characters, being for the most part volatile liquids of aromatic odour, and very slightly soluble in water, though generally miscible with alcohol in all proportions. Comparatively few are crystallisable. Among the most interesting examples of crystallisable ethereal salts are the constituents of the natural fats:—



Palmitin or glyceric palmitate

$$\left.\begin{matrix} C_{15}H_{31}.CO.O \\ C_{15}H_{31}.CO.O \\ C_{15}H_{31}.CO.O \end{matrix}\right\rangle (C_3H_5)'''$$

and

Stearin or glyceric stearate

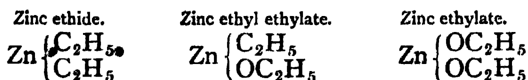
$$\left.\begin{matrix} C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \\ C_{17}H_{35}.CO.O \end{matrix}\right\rangle (C_3H_5)'''$$

The decomposition of these and similar compounds by alkalies constitutes the process of *saponification.*

8. ORGANO-METALLIC COMPOUNDS.

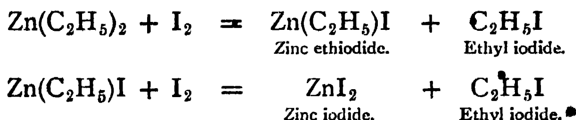
These are compounds of metals or metalloids with hydrocarbon radicles. They are volatile, very oxidisable, and generally heavy liquids. The zinc-ethyl compound was first obtained. It is a colourless liquid, boiling at 118°, and spontaneously inflammable when thrown into the air. It is

instantly decomposed by water, and when submitted to the action of successive small quantities of oxygen it yields two oxidised compounds, thus :—



Zinc ethide.	Zinc ethyl ethylate.	Zinc ethylate.
$Zn\begin{cases}C_2H_5\\C_2H_5\end{cases}$	$Zn\begin{cases}C_2H_5\\OC_2H_5\end{cases}$	$Zn\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$

Iodine removes from it half and then the whole of the ethyl, according to these equations :—



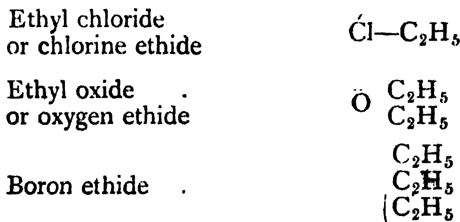
$$Zn(C_2H_5)_2 + I_2 = \underset{\text{Zinc ethiodide.}}{Zn(C_2H_5)I} + \underset{\text{Ethyl iodide.}}{C_2H_5I}$$

$$Zn(C_2H_5)I + I_2 = \underset{\text{Zinc iodide.}}{ZnI_2} + \underset{\text{Ethyl iodide.}}{C_2H_5I}$$

The existence of these compounds furnishes conclusive testimony to the diadic character of the zinc atom, and in other cases similar evidence, of great value in settling questions relating to valency and atomic weight, has been obtained by the study of these compounds.

The following are the formulæ of some of the most interesting organo-metallic compounds. It will be noticed that they are constituted in the same way as the chlorides and oxides of the same hydrocarbon radicles, the special peculiarities of the organo-metallic compounds being due to the unoxidised condition of the metals they contain.

The vapour densities of all these compounds are normal, so that each formula represents two volumes of vapour.



Ethyl chloride or chlorine ethide	$Cl—C_2H_5$
Ethyl oxide . or oxygen ethide	$O\begin{cases}C_2H_5\\C_2H_5\end{cases}$
Boron ethide .	$\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases}$

Silicon ethide . . .	$\overset{iv}{Si}\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$
Trimethyl arsine . . or arsenious trimethide .	$\overset{\prime\prime\prime}{As}\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$
Diarsenious tetramethide . (kakodyl)	$\left\{\begin{matrix}\overset{\prime\prime\prime}{As}(CH_3)_2\\\overset{\prime\prime\prime}{As}(CH_3)_2\end{matrix}\right.$
Trimethyl stibine . . or antimonious trimethide .	$\overset{\prime\prime\prime}{Sb}\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$
Triethyl bismuthine . . or bismuthous triethide .	$\overset{\prime\prime\prime}{Bi}\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$
Zinc ethide . . .	$Zn\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$
Mercuric ethide . .	$Hg\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$
Stannous ethide . .	$\overset{\prime\prime}{Sn}\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$
Stannic ethide . . .	$\overset{iv}{Sn}\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$
Plumbic ethide . .	$\overset{iv}{Pb}\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right.$

EXERCISES ON SECTION II.

1. What experiments and reasoning would lead you to regard chlorine as a monad element?

2. In what respects does iodine resemble and differ from bromine?

3. Discuss the title of hydrogen to be considered (*a*) a non-metal; (*b*) a metalloid.

4. Classify the solid elements according to their relative densities.

5. What are the properties which distinguish chlorine, and the elements most like chlorine, from potassium, and the elements which are most like potassium?

6. Compare and contrast the elements phosphorus and arsenic, both in their physical and chemical properties.

7. What are the special characteristics of carbon which distinguish it from other elements?

8. Describe as many as you can of the modified forms of carbon, sulphur, and phosphorus.

9. What acids are known consisting of hydrogen, oxygen, and phosphorus? Give their graphic constitutional formulæ, and point out the basicity of each.

10. What resemblances and differences are observable between the corresponding compounds of potassium and sodium?

11. To what elements does mercury present the greatest resemblance? Point out instances of analogy in properties.

12. Show by a comparison of their compounds in what respects the elements carbon, silicon, tin, and lead may be said to constitute a natural group.

13. Give the formulæ, simple and constitutional, of the following compounds: common salt, caustic potash, sulphuric acid, baryta, barium peroxide, lead peroxide, iron peroxide, silver phosphate, silver arsenate, silver arsenite, kakodyl, and tartar-emetic.

14. Give a full account of the two oxides of nitrogen known as nitric oxide and nitric peroxide respectively.

15. Give instances of compounds which do not comply with the law of even numbers.

16. What are the chief points of resemblance and difference between the corresponding calcium and magnesium compounds?

17. Assign a place among the elements to each of the following bodies: copper, nitrogen, boron, thallium, vanadium, gold. Give full reasons in each case.

18. The constitution of phosphorus compounds has been explained on the assumption of the trivalence of the phosphorus atom. Discuss this view.

19. By what arguments would you support the number 32 against the number 16 as the atomic weight of sulphur?

20. Tabulate the physical and chemical properties of tin and lead so as to explain their association in the periodic scheme.

21. What is an alum? At the temperature of 180° common alum loses $\frac{23}{24}$ of its water. How may this fact be brought to bear upon the construction of its formula?

22. Classify some of the better known elements according to their valency, mentioning and explaining, so far as possible, doubtful cases.

23. Write the formulæ of orthosulphuric acid and some of its salts. An ortho-acid may be defined as one in which the characteristic element (sulphur in this case) is saturated with hydroxyl.

24. One gram of phosphorus yields 2·2903 grams of phosphoric anhydride. Will this enable you to determine the atomic weight of the element? and, if not, what further data are necessary?

25. How much phosphorus is contained in 120 lbs. of bone-ash, consisting of $Ca_3(PO_4)_2$ 88·5 parts and $CaCO_3$ 11·5 parts in 100?

26. What weight of phosphorus is contained in 10 litres of phosphorus vapour at 1040°? Pressure normal.

27. What weight of phosphorus is contained in 10 litres of phosphine at 12°? Pressure normal.

28. Write the formulæ of a few 'molecular' compounds and consider in each case whether the compound can be reasonably represented by a single unitary formula.

29. Calculate the percentage composition of cryolite, Na_3AlF_6.

30. How many kilograms of litharge can be obtained from 40·5 kilos. of lead, and what volume of oxygen measured at 20° and under 765 mm. is absorbed in the process?

31. Write down the formulæ of all the possible silver salts of the following acids:—


$HClO_3$, $HClO_4$, H_2SO_4, H_3PO_4, H_4SiO_4, H_2SO_3, H_3PO_3.

32. Write down the formulæ for all the chlorides and amides theoretically derivable from the following acids:—


HNO_3, H_2SO_4, $H_4P_2O_7$, $HC_7H_5O_2$ (benzoic acid, monobasic).

33. Write the constitutional formula of Nordhausen sulphuric acid, $H_2S_2O_7$, and of chromic acid, H_2CrO_4, assuming sulphur and chromium hexad.

34. Write down the formulæ for the possible anhydrides derived from orthosulphuric acid, $S(OH)_6$, by successive stages of dehydration.

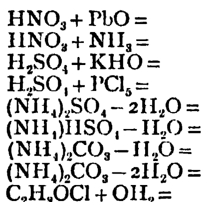
35. Give the formulæ for the anhydrides corresponding with sulphuric acid, H_2SO_4, phosphoric acid, H_3PO_4, pyrophosphoric acid, $H_4P_2O_7$, nitric acid, HNO_3, nitrous acid, HNO_2, hyponitrous acid, $H_2N_2O_2$, thiosulphuric acid, $H_2S_2O_3$, chloric acid, $HClO_3$, perchloric acid, $HClO_4$, and acetic acid, $HC_2H_3O_2$, pointing out those which are actually known.

36. Give concise definitions of the terms acid, base, salt, with examples of their characteristic properties drawn from your own experience.

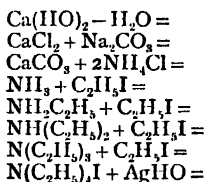
37. How would you explain the terms acid, and neutral salt? Give examples.

38. A number of salts having the general formula $M'HSO_2$ were called by the discoverer hydrosulphites. What name should they bear according to the rules laid down in Chap. IV.? Write the graphic formulæ for these bodies, and mention compounds which are similarly constituted.

39. Complete the following equations, adding the name to each formula :—



$HNO_3 + PbO =$
$HNO_3 + NH_3 =$
$H_2SO_4 + KHO =$
$H_2SO_4 + PCl_5 =$
$(NH_4)_2SO_4 - 2H_2O =$
$(NH_4)HSO_4 - H_2O =$
$(NH_4)_2CO_3 - H_2O =$
$(NH_4)_2CO_3 - 2H_2O =$
$C_2H_3OCl + OH_2 =$



$Ca(HO)_2 - H_2O =$
$CaCl_2 + Na_2CO_3 =$
$CaCO_3 + 2NH_4Cl =$
$NH_3 + C_2H_5I =$
$NH_2C_2H_5 + C_2H_5I =$
$NH(C_2H_5)_2 + C_2H_5I =$
$N(C_2H_5)_3 + C_2H_5I =$
$N(C_2H_5)_4I + AgHO =$

40. Give reasons in favour of each of these formulæ for sal-ammoniac :—



NH_3HCl
NH_4Cl

41. To which class of compounds would you refer the following substances?

Caustic potash, KHO ; lime, CaO ; nitrous oxide, N_2O ; nitrogen trioxide, N_2O_3 ; ferric oxide, Fe_2O_3 ; chromium trioxide, CrO_3 ; wood spirit, $CH_3.OH$; glycerine, $C_3H_5(OH)_3$; urea, $CO(NH_2)_2$.

42. Accepting the formula HCl for hydrochloric acid, what facts determine the choice of the formula $H_2C_2O_4$ for oxalic acid?

43. How far do the following compounds agree with definitions of the terms acid, base, salt? Give sufficient reasons in each case.

Chlorides of hydrogen, potassium, aluminium, phosphorus, sulphur; oxides of hydrogen, potassium, carbon; hydroxides of potassium, aluminium, arsenic, silicon.

44. Define the terms hydrate and hydroxide. Classify the following compounds :—



$$Cl_2.10H_2O, \quad KHO, \quad H_3AlO_3, \quad C_2H_5OH.$$

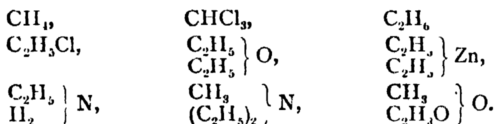
45. Write the constitutional formula of urea, and of the compound with which it is isomeric.

46. How many litres of marsh-gas would be equal in weight to 25 litres of ethylene?

47. Benzoate of silver has the formula $C_7H_5AgO_2$. Calculate its percentage composition, also the weight of silver contained in ·5736 gram of this salt.

48. From the formulæ HBr, H_2S, CCl_4, NH_4Cl, H_2SO_4, state the valence of the symbols Br, S, C, N, and S, giving your reasons in each case.

49. Name and classify the following compounds :—



CH_4,	$CHCl_3$,	C_2H_6
C_2H_5Cl,	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$,	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn$,
$\left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}N$,	$\left.\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}\right\}N$,	$\left.\begin{matrix}CH_3\\C_2H_3O\end{matrix}\right\}O$.

50. Assign a formula to a body containing C 26·6, H 2·2, and O 71·1 per cent.

51. How would you prove that the formula of marsh-gas is CH_4? Also, how could you show that ethylene contains twice as much carbon?

52. Give reasons for representing oxalic acid as $C_2H_2O_4$, not CHO_2; acetic acid as $C_2H_4O_2$, not CH_2O; ethylene as C_2H_4, not CH_2.

53. By what experiments could you prove that the molecule of benzene is correctly represented by the formula C_6H_6, not C_3H_3?

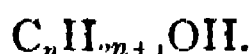
54. A body having the composition $C_5H_{12}O$ is an alcohol. Express by equations the probable action upon it of acetic acid, oxalic acid, and oxidising agents.

55. The compound C_4H_8O is either an aldehyd or a ketone: how would you recognise its true character? Write out the constitutional formula of the aldehyd and ketone of this composition, and indicate the constitution of any metameric modification that may exist.

56. Dissect the crude formula $C_7H_{14}O_2$, showing the nature of the several metameric compounds which it may represent.

57. In respect of what properties may you regard alcohols as water molecules in which hydrogen has been replaced by hydrocarbon radicles? Illustrate by reference to common alcohol, C_2H_5OH.

58. The ethylic series of monohydric alcohols are represented by the general formula—



$$C_nH_{2n+1}OH.$$

Write out the formulæ for the corresponding aldehyds, acids, and acetic derivatives (acetates).

59. How many acids could be derived from the alcohol—



$$\begin{cases} CH_2.OH \\ CH_2.OH, \end{cases}$$

and what would be their formulæ?

60. Carbolic acid is sometimes called phenylic alcohol. In what respects do its alcoholic properties differ from those of the alcohols of the ethylic series, $C_nH_{2n+2}O$?

61. Complete these equations:—



$$CH_3.CO(OH) + PCl_5 =$$
$$CH_3.OH + HCl =$$
$$\left.\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\} O + 2HCl =$$
$$2CH_3.CO(OH) + Ag_2O =$$
$$CH_3.OH + \left.\begin{matrix} C_2H_5O \\ HO \end{matrix}\right\} SO_2 =$$
$$CH_3.CO(OCH_3) + NaHO =$$
$$\left.\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\right\} O + H_2O =$$

62. In what respect does prussic acid resemble and how does it differ from hydrochloric and hydrobromic acids?

63. ·3339 gram of a compound gave ·7896 gram of CO_2 and ·2924 gram H_2O. The vapour density (air = 1) was found to be 6·59. Calculate a rational formula.

64. ·1483 gram of ethylated acetone gave ·3799 gram of CO_2 and ·1575 gram of water. Its vapour density (air = 1) was 2·951. Calculate the formula of the compound.

65. The analysis of barium diacetotartrate gave the following results:—

I. ·2065 gram of substance gave ·1297 gram of $BaSO_4$.

II. ·1377 gram of substance gave ·1307 of CO_2 and ·0300 of H_2O.

Calculate the formula of the salt and of the corresponding acid.

66. The following results were obtained in the analysis of the copper salt of ethyl-benzoic acid: ·2218 gram gave ·4827 gram of CO_2, ·1004 gram of water, and ·0489 gram of CuO. Calculate the formula of the acid.

SECTION III.

CHEMICAL KINETICS.

CHAPTER XVII.

CONDITIONS OF CHEMICAL CHANGE.

IN considering the general conditions under which chemical changes are brought about, it is necessary to distinguish between those which, on the one hand, are *essential* to the act of combination between two or more substances presented to each other, or to the occurrence of other kinds of change, and those which, on the other hand, affect the *rate* at which a given change proceeds, or the *extent* of its action.

I. Under the first division there are two principal conditions which must in all cases be fulfilled. Bodies act upon each other chemically only when, according to the usual phrase, they are in absolute contact; that is to say, when they are so near to each other that the distance between them is too small to be observed. What this distance is depends probably upon the nature of the substances concerned, but its measure is probably of the same order of magnitude as the dimensions of a molecule, or when a solid is concerned, the limited distance through which the molecules on the surface are able to move.

In this respect chemical attraction differs from the attraction of gravitation, and of electrical and magnetic induction, all of which are capable of operating through distances

which are appreciable by our senses and measurable by our instruments. On the other hand, it agrees thus far with *cohesion*, in virtue of which the molecules of bodies are held together in masses, and with *adhesion*, which causes surfaces of various kinds after being closely approximated to remain united.

Some cases of action in which it appears at first sight that this condition of contact is not fulfilled are only apparent. Solid phosphorus and solid iodine laid near to each other, but not actually touching, do combine; but this is due to the fact that at common temperatures both emit vapour, and, the vapours meeting, unite. That this is the explanation is shown by the fact that these two substances may be left even in contact with each other for some time, if they are both cooled to a temperature of about —20°. This brings us to the consideration of the second condition which is essential to chemical action, namely, the observance of a certain range of temperature, above or below which no action will take place.

Moderate elevation of temperature generally favours chemical combination, and is very often indispensable. Thus it is a familiar fact that ordinary combustibles—wood, coal, gas, and even sulphur and phosphorus—do not begin to burn unless the temperature of some part of the mass is raised sufficiently. Iron and sulphur have no action on each other at common temperatures; copper has no action on sulphuric acid unless heated to about 130°, and so in many other cases. By cooling the materials, chemical changes that would otherwise occur may be delayed or prevented altogether. At the temperature of liquid air or liquid oxygen, about —182°, all chemical combinations between substances usually highly reactive are suspended. Phosphorus and bright sodium are alike unaffected by contact with the liquid or with chlorine or bromine which at that temperature are in the solid state. Cooling, however, does not in any case cause decomposition, and many chemical

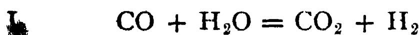
compounds can only be formed and continue to exist at moderately low temperatures. Thus many salts unite with water and with ammonia to form definite chemical compounds which are readily destroyed by heat. Phosphine PH_3 and hydrogen chloride when under atmospheric pressure will combine to form phosphonium chloride only when cooled considerably below atmospheric temperature. In such cases the tendency of one or other of the components to assume the gaseous state is, of course, an important factor in the change.

On the other hand, while in most cases a moderate elevation of temperature is necessary to initiate chemical action, if the temperature is high enough combination is prevented. Thus, while mercury is indifferent to oxygen at all temperatures up to about 300°, combination then ensues, but the oxide is broken up at a low red heat, and mercury vapour and oxygen at temperatures of about 700° and upwards are without action on each other. The temperatures at which various elements cease to act on one another are very different, but usually very high, and do not admit of exact measurement. It is probable that hydrogen and oxygen cease to combine at about 3000° C.

There is a third condition which is by some chemists regarded as essential to the establishment of chemical action between two bodies, and that is the presence, it may be in minute quantity, of a third substance. This hypothesis is based on the observation of many striking examples, but its establishment as a general proposition will require much more knowledge of the facts than we at present possess. It has long been known that chlorine is without action on sodium or on copper when both the gas and the metal are perfectly clean and dry. More recent experiments have shown that many other substances, which under ordinary circumstances interact, have no action upon one another in the absence of moisture. For example, dry hydrogen chloride and dry ammonia do not form ammo

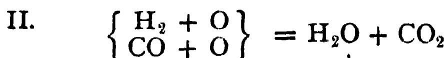
nium chloride; and, on the other hand, dry ammonium chloride does not split up as usual when heated to 350°. Dried ammonium chloride may be sublimed from a mixture of the salt with dried lime without the evolution of ammonia. And even phosphorus and charcoal can scarcely be made to burn in dried oxygen. A mixture of dry carbonic oxide and oxygen does not explode when an electric spark is passed through it, but the addition of a minute trace of water vapour makes the mixture explosive, and the rapidity of the explosion increases with the quantity of steam introduced. The presence of a minute quantity of various gases which contain hydrogen, such as hydrogen sulphide and chloride, ether vapour, or pentane, has a similar effect; but the addition of dry nitrous oxide or carbon disulphide was not found to render the mixture inflammable.

Why steam and hydrogen compounds, which by interaction with oxygen produce steam, should be necessary for the propagation of the flame through the gas has not been fully explained. Probably at the temperature of the spark the water molecule is less stable than the oxygen molecule, and the decomposition expressed by equation I occurs.



$$\text{I.} \qquad CO + H_2O = CO_2 + H_2$$

The second phase may be an example of the effect of two attractions acting concurrently, the hydrogen and carbonic oxide in equation II dividing a molecule of oxygen between them, and the H_2O then reacting with another molecule of CO, and so alternately.

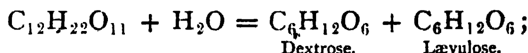


$$\text{II.} \qquad \left\{ \begin{matrix} H_2 + O \\ CO + O \end{matrix} \right\} = H_2O + CO_2$$

Other substances, however, have long been known to play a part, which is usually spoken of as 'catalytic,' similar that of water in the cases just cited. One of the most miliar of these is the rapid decomposition of potassium

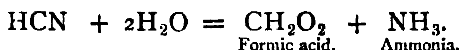
chlorate by heat in the presence of a small quantity of manganese dioxide, ferric oxide, or cupric oxide, and the somewhat similar evolution of oxygen from bleaching powder by the action of a little oxide of cobalt.

Deacon's process for making chlorine—viz. by passing a mixture of air and hydrogen chloride over a heated copper salt—is another example of the same kind of effect. So also is the action of a small quantity of acid in promoting the hydrolysis of such compounds as cane sugar—



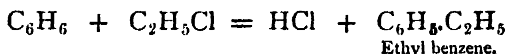
$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6};$$

and the elimination of the nitrogen of cyanides and isocyanides—



$$HCN + 2H_2O = \underset{\text{Formic acid.}}{CH_2O_2} + \underset{\text{Ammonia.}}{NH_3}.$$

Another example is afforded by the application of aluminium chloride in promoting union of hydrocarbon radicles; as, for instance, when added to a mixture of benzene and ethyl chloride, which otherwise have no action on each other:—



$$C_6H_6 + C_2H_5Cl = HCl + \underset{\text{Ethyl benzene.}}{C_6H_5.C_2H_5}$$

In all these cases there is strong probability in favour of the hypothesis that the action proceeds through a cycle, an unstable compound being formed in small quantities at a time and subsequently decomposed the 'catalyst,' as the active substance may be called, returning finally to the same state of combination as at first.

II. Turning now to those agencies which, though not always indispensable to chemical combination or interaction, are found to increase the rate and affect the extent of chemical action. The first and most familiar is elevation of temperature, but it is not always possible to explain the great increase in the rate of action which is observed on

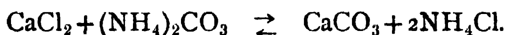
raising the temperature a few degrees. Hydrochloric acid, for example, acts very slowly upon metallic tin at the temperature of the air, but when heated to near boiling point the action is fairly rapid. In such a case part of the effect may be due to increased molecular motion in the liquid; partly to convection currents which bring fresh portions of acid rapidly into contact with the metal; partly, also probably, to increased ionic action (see Chap. XIX.), though in the case of a strong acid, like hydrochloric acid, this contributes only a small part of the total effect.

Another influence which frequently operates when metals are concerned is the electrical condition of the surface in contact with the reagent. In the case of tin and hydrochloric acid, for example, the dissolution of the tin is greatly promoted if a few pieces of platinum foil are mixed with the metal, for then the conditions of a voltaic circuit are established, the platinum being the negative surface and the tin the positive, electrolysis of the acid proceeding much more quickly than in the absence of the platinum. The same principle is acted upon in many laboratory operations, as, for example, in the 'copper-zinc couple' which is used in the presence of water as a reducing agent, and the addition of platinic chloride to the acid used in the generation of hydrogen by means of pure zinc, whereby a minute quantity of platinum is distributed over the surface of the metal. The electrochemical effect of permitting such metals as iron or zinc to remain in contact with less positive metals, such as tin, or even with the oxides of the metals themselves, is often neglected, with the result that the decay of such metals when exposed to air and water is greatly promoted.

The mechanical condition of bodies also has an important influence. Though in a few cases solids may be made to combine together by subjecting them to powerful pressure, or by continued trituration, union occurs only at their surfaces of contact, and cannot be completed unless

one of the bodies, at least, is in the liquid or in the gaseous state. That is to say, the several parts of the acting masses must be free to move so that the mutual interpenetration required for chemical combination may be perfect.

The nature of the solvent or medium in which two bodies are presented to each other often influences their mutual action ; and the physical character of the products as to fusibility or volatility frequently determines whether, and in what manner, chemical action may occur. Thus, when calcium chloride and ammonium carbonate are dissolved in separate portions of water, and the solutions then mixed together, a precipitate of calcium carbonate is thrown down and ammonium chloride remains in the liquid. But if the liquid is boiled for some time the greater part of the calcium carbonate passes again into solution, while ammonium carbonate escapes in vapour. The same change occurs completely if the two salts, calcium carbonate and ammonium chloride, are mixed together in the dry state and are heated. The interaction is one which is usually spoken of as reversible, and to indicate its reversibility under change of conditions the equation may be written in the following manner :—



$$CaCl_2 + (NH_4)_2CO_3 \rightleftarrows CaCO_3 + 2NH_4Cl.$$

Again, if acetic acid is poured into an aqueous solution of potassium carbonate, effervescence ensues from the escape of carbon dioxide and a solution of potassium acetate is formed. But if potassium acetate is dissolved in strong spirit of wine, a liquid in which potassium carbonate is insoluble, a stream of carbon dioxide transmitted through the solution is capable of throwing down a precipitate of potassium carbonate, leaving acetic acid in solution.

We may accept it as very generally true, that when we mix together two soluble salts, which by double decomposi-

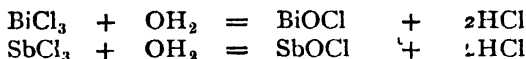
tion are capable of giving rise to an insoluble compound, that insoluble compound will be precipitated until complete decomposition of one or both the generating salts has taken place. If, for example, we take the two salts, barium chloride and sodium sulphate, knowing beforehand that barium sulphate is insoluble in water, we may safely assert that a precipitate will be formed when the aqueous solutions of these two salts are mixed together.

Such changes, however, are merely special cases of the general rule concerning all acids, bases, and salts, which are included under the general term electrolyte (see Chap. XIV.). Barium salts in solution yield Ba ions abundantly, and sulphates in solutions yield SO_4 ions. Neither are completely dissociated, but each solution contains a small amount of undivided molecules. Barium sulphate, though nearly insoluble in water, is not absolutely so; its solution therefore contains Ba and SO_4 ions with some $BaSO_4$. By increasing the number of Ba and SO_4 ions in the liquid, the excess of $BaSO_4$ beyond its solubility limit leads to the precipitation of all the excess in the form of solid barium sulphate.

Similar observations hold good with regard to mixtures of compounds which, amongst them, contain the elements of a gas or substance volatile at the temperature of the experiment. In many cases this volatile substance is formed. Conversely, if we submit to pressure or to a very low temperature a mixture of substances which, under ordinary atmospheric conditions, evolves a gas, the chemical action is retarded, or sometimes prevented altogether.

When several bodies capable of acting on one another are mixed together, but the quantity of one of them largely preponderates over the rest, some curious results are frequently brought about. When, for example, a solution of bismuth or antimony chloride in ordinary aqueous hydrochloric acid is mixed with a little water, no change in perceptible to the eye, but the addition of a larger quantity of

water throws down a white precipitate of the oxychloride, $BiOCl$ or $SbOCl$. These decompositions take place according to the following equations :—



$$BiCl_3 + OH_2 = BiOCl + 2HCl$$
$$SbCl_3 + OH_2 = SbOCl + 2HCl$$

That is to say, one molecule or 18 parts by weight of water decompose one molecule or 314·5 parts of bismuth chloride, or 226·5 parts by weight of antimony chloride; and yet, if these proportions of the materials are brought into contact, only a partial decomposition takes place, and the reaction is completed only when a much larger quantity of water is added. In such a change as this we must remember that there are two antagonistic agents at work, namely, the water tending to decompose the chloride according to the equations given above, and the hydrogen chloride which is generated by that decomposition tending to reproduce the chloride. We may, therefore, consider that there are four compounds in presence of one another, and surrounded by water molecules.

Taking one case,

We have $BiCl_3$, OH_2, $BiOCl$, and HCl.

We may safely assume that when the number of water molecules present is augmented, the number of molecules of chloride decomposed by water in a given interval will increase, whilst the number of oxychloride molecules decomposed by the hydrochloric acid present will *pari passu* diminish, until the whole of the chloride is destroyed and precipitation is complete.

If now to the liquid holding the precipitate in suspension we add hydrochloric acid in excess the action is reversed, and the precipitate disappears again.

In such operations the change proceeds continuously as the quantity of the acting body is increased, any alteration in the proportions, however small, being followed by

corresponding alteration in the extent of the interaction. This is only another way of expressing the law of *mass-action*, which states that the rate and the amount of change between any two bodies in a solution or in the gaseous state is proportional to the product of the active masses and of a constant which is the measure of affinity and varies with the materials concerned. By active mass is generally meant the number of molecules of each reagent in unit volume.

Similar actions and reactions ensue when salts in solution are mixed together, or when acids are mixed with salts, with alcohols, or with ethers, and generally when several substances meet together, the final condition of equilibrium being attained after a lapse of time, which in some cases is long enough to be measurable.

In the early attempts to apply the law of Avogadro to the determination of molecular weights, many cases of 'abnormal vapour density' presented themselves and gave rise to much controversy. Thus sulphuric acid is entirely vaporisable at a moderate temperature, but the relative density of the vapour of this compound is only about one-fourth, and not one-half, of the molecular weight as represented by the formula H_2SO_4, which accords with the bibasic character of sulphuric acid. In other words, vapour of sulphuric acid instead of being, in accordance with the general rule, forty-nine times as heavy as an equal volume of hydrogen taken at the same temperature, is only $\frac{49}{2} = 24\frac{1}{2}$ times as heavy or thereabouts.

Ammonium chloride, phosphorus pentachloride, and calomel afford instances of the same kind.[1] These anomalies are explained by the hypothesis that when these compounds are volatilised they are at the same time resolved into two distinct products; sulphuric acid into sulphur trioxide and water, ammonium chloride into ammonia and hydrogen chloride, phosphorus pentachloride into phosphorus trichlo-

[1] Ammonium chloride and calomel, and probably also phosphorus pentachloride, when completely dried give normal vapour densities.

ride and chlorine, calomel into mercuric chloride and mercury. And in these particular cases direct experimental evidence can be adduced that these products exist in the several vapours.

In the case of sulphuric acid and of ammonium chloride advantage has been taken of the difference in the diffusibility of the products of decomposition. Thus the vapour of sulphur trioxide is much heavier and consequently less diffusible than vapour of water, so that when sulphuric acid is heated for several hours in a vessel with a capillary orifice, the water vapour escapes more rapidly than the sulphur trioxide, and the latter gradually accumulates in the residue. Pentachloride of phosphorus has also been resolved into free chlorine and phosphorus trichloride, which may be to some extent separated by diffusion.

In the case of sublimed calomel we can appeal to the fact, well known to manufacturers, that it invariably contains small quantities of corrosive sublimate, and of metallic mercury, which have escaped recombination during the cooling down of the vapour.

Decompositions of this kind are, like others already referred to, reversible by changing the conditions, and they afford examples of *dissociation*, or, as it is sometimes more precisely termed, *thermolysis*.

Direct proof that dissociation has occurred is not possible in all cases, though there is usually some collateral evidence available in support of the natural inference from the vapour density. An interesting case is presented by the halogens, especially iodine. The vapour density of this element at temperatures up to about 700° is 8·8 (air = 1); above 700° the density diminishes rapidly, being reduced at 1500° (the pressure being ·3 atmosphere) to nearly half this, or 4·6. The conclusion seems to be inevitable that at the lower temperature molecules of iodine consist of two atoms I_2, whilst at the higher they dissociate into separate atoms.

In accordance with the doctrine of atomic and molecular motion already explained, the phenomena of dissociation result from two opposite and reciprocal actions—the one of decomposition, the other of recombination proceeding simultaneously. At low temperatures, when the composition of hydrogen sulphate, for example, is represented by the formula H_2SO_4 or H_2O,SO_3, the number of molecules decomposed, into H_2O and SO_3, is exactly counterbalanced by the number of molecules which are reconstituted in the same period by the reunion of these two substances. As the temperature rises and the agitation of the molecules in the mass becomes more vigorous, the number of molecules which undergo decomposition progressively increases, whilst the recombination *pari passu* continually decreases, till at length a point is reached in which the SO_3 molecules and the OH_2 molecules become indifferent to each other, and recombination no longer takes place. When the temperature is allowed to fall these processes are reversed, and for every degree of temperature a certain definite relation subsists between the decomposition and recomposition, so that equilibrium is maintained. The compensating process being at high temperatures annulled, decomposition is complete; the vapour consists throughout of a uniform mixture of two different kinds of molecules, and consequently, by the law of Avogadro, it occupies twice the volume it would otherwise fill if dissociation did not take place.

The cases just considered and others which might be quoted, such as the phenomena exhibited by nitric peroxide NO_2 or N_2O_4, involve only one physical condition or phase in the substances concerned. But in many cases the process of dissociation results in the production of a vapour with a residue of solid. Thus when calcium carbonate is heated strongly it suffers decomposition into lime, which remains behind together with calcium carbonate, while carbon dioxide gas is given off. This change proceeds until the evolved gas acquires a certain density or pressure, and

it then ceases till the temperature or the pressure is changed. Similarly salts which contain water of crystallisation, when heated evolve water vapour, leaving a residue of salt more or less dehydrated.

The same kind of decomposition takes place in many cases at the temperature of the air, and under ordinary conditions. Salts, which thus readily part with their water of crystallisation and fall away to powder, are said to be *efflorescent*. Sulphate, carbonate, and phosphate of sodium afford examples of this kind of dissociation, which, however, presents nothing remarkable beyond the fact of occurring at comparatively low temperatures. In this respect, however, these phenomena are surpassed by those exhibited by salts, which, under ordinary circumstances, are deposited from solution void of water of crystallisation. Such compounds combine with water when crystallised at temperatures below zero. The explanation of the existence of anhydrous crystals is simply that dissociation of the salt from the water occurs at or below the temperature at which the crystals are deposited. And even those salts which usually combine with water of crystallisation may be obtained in a lower state of hydration, or altogether destitute of water, by causing them to crystallise at more or less elevated temperatures. Sodium sulphate furnishes a case in point. The crystals of this salt formed at ordinary temperatures contain ten molecules of water of crystallisation combined with one of the salt ($Na_2SO_4.10OH_2$) ; when formed at 18° they contain seven molecules of water ($Na_2SO_4.7OH_2$), whilst a solution heated to 34° yields crystals which contain no water at all. In these, as in all other cases, the dissociation may be regulated not only by change of temperature but by altering the concentration of any product of the decomposition. Thus the decomposition of calcium carbonate by heat may be completely prevented by increasing the pressure of the carbon dioxide, and practically in the working of a limekiln it is found that the limestone may be heated, even till it melts, without being

converted into lime, unless the kiln is well ventilated and the carbon dioxide carried off by a current of air as fast as it is produced. Similarly efflorescent salts will preserve their water of crystallisation in an atmosphere saturated with water vapour, and if phosphorus pentachloride is mixed with a sufficient quantity of the trichloride PCl_3, it gives a vapour the density of which is very nearly normal, that is, it corresponds with the formula PCl_5.

An excellent example of the influence of pressure is afforded by the behaviour of the phosphonium salts. At ordinary atmospheric temperatures and pressures the iodide PH_4I is alone capable of retaining the solid state; the bromide, though obtainable temporarily in cubes, evaporates away very rapidly; the chloride is only producible by compressing a mixture of equal volumes of PH_3 and HCl at about twenty atmospheres or by cooling at atmospheric pressure to $-25°$. Crystals of the last compound instantly disappear into a mixture of the two gases on release of the pressure when the temperature is that of the air.

The rate and extent of dissociation in a given case therefore, independently of the chemical character of the substance concerned, depend upon three conditions; namely, (1) temperature, (2) pressure, and (3) the proportion of the products of dissociation to the undecomposed substance. A parallel may be traced between the phenomena of dissociation and of evaporation, or, in other words, between the separation of molecules and atoms of different kinds and the separation of molecules of the same kind in passing under the influence of heat or diminished pressure from the solid or liquid to the gaseous state. The vaporisation of water from a crystallised salt, for example, seems to be a phenomenon of the same order as the escape of water vapour from ice. In all such cases the rate of vaporisation is governed by temperature and pressure, and is attended by absorption of the energy of heat, while reversal of the con-

ditions leads to a restoration of the substance to its original state.

Molecule of substance before dissociation.	Products of complete dissociation at t°.	t° approximately. Pressure 1 atmos.
I_2 vapour below 700°	$I + I$	1500°
Br_2 vapour	$Br + Br$	1500°
Cl_2 gas	$Cl + Cl$	above 1600°
S_6 vapour at 482°	$S_2 + S_2 + S_2$	940°
N_2O_4 vapour below 0°	$NO_2 + NO_2$	160°
$[N_2O_4]_n$ liquid	$NO_2 + NO$ vapour	all temps.
PCl_5 b.p. 160°–165°	$PCl_3 + Cl_2$	300°
$SbCl_5$	$SbCl_3 + Cl_2$	
$[Hg_2Cl_2]_n$ solid	$HgCl_2 + Hg$ vapour	950°
$[Al_2Cl_6]_n$ solid	$AlCl_3 + AlCl_3$ vapour	800°
$[ICl_3]_n$ solid	$ICl + Cl_2$ vapour	all temps.
H_nF_n vapour at 20°	$HF + HF$	90°
$[NH_4Cl]_n$ solid	$NH_3 + HCl$	350° to 940°
$[NH_4Br]_n$ solid	$NH_3 + HBr$	440° to 772°
$[NH_4I]_n$ solid	$NH_3 + HI$	440° to 772°
$[PH_4I]_n$ solid	$PH_3 + HI$	
$[(C_2H_5)_4NI]_n$ solid (tetrethylammonium iodide)	$(C_2H_5)_3N + C_2H_5I$ vapour (triethylamine + ethyl-iodide)	all temps.
$[NH_4HS]_n$ solid	$NH_3 + H_2S$	57°
$[H_2SO_4]_n$ liquid	$H_2O + SO_3$	416°
$[C_5H_{11}Cl]_n$ liquid (isoamyl chloride)	$C_5H_{10} + HCl$ (amylene)	300°
$[SCl_4]_n$ liquid at −22°	$SCl_2 + Cl_2$	8°
$[C_2H_3Cl_3O_2]_n$ solid, boils 95° (chloral hydrate)	$C_2HCl_3O + H_2O$ (chloral)	100°
$[C_2H_2(C_2H_5)Cl_3O_2]$ solid (chloral-alcoholate)	$C_2HCl_3O + C_2H_6O$ (chloral + alcohol)	116°
$[C_2H_4O_4 + CH_2O_2] = 4$ vols. (formic acid vapour at b.p. 101°)	$CH_2O_2 + CH_2O_2 + CH_2O_2$ (formic acid)	220°
$[C_4H_8O_4 + C_2H_4O_2] = 4$ vols. (acetic acid vapour at b.p. 119°)	$C_2H_4O_2 + C_2H_4O_2 + C_2H_4O_2$ (acetic acid)	250°
Solid compounds of salts with ammonia, *e.g.* $[AgCl.3NH_3]_n$	Salt + nNH_3	
Salts united with water of crystallisation.	Anhydrous salt + nH_2O	

CHAPTER XVIII.

THERMAL EFFECTS OF CHEMICAL ACTION.

EVERY chemical change, whether it occurs in one substance alone or as a result of the contact of two or more substances, is attended by a redistribution of the total energy of the system. This is most commonly manifested in the form of absorption or evolution of heat. There is, however, nothing in this to distinguish chemical change from physical or mechanical changes, such as fusion, vaporisation, or alteration of density.

Suppose a mass of ice at 0° to be so gradually heated that it melts, but the resulting water remains at the same temperature. The amount of energy in the form of heat thus supplied would raise the temperature of the same mass of water from 0° to 80°. If the mass of ice is a gram we say that 80 thermal units, or 80 units of heat, or 80 calories, are required for its fusion.[1] In similar terms 100 units are required to raise the temperature of a gram of water from 0° to the boiling-point under a pressure of one atmosphere, and 537 units more to change it into steam. At a much higher, unknown, temperature the disruption of one gram of water gas into a mixture of hydrogen and oxygen would require at least 3,780 units, and probably much more. All these changes are reversible, and when reversed the same quantities of heat are successively given out.

The more obviously chemical changes which have been studied in relation to the thermal changes which attend them may be ranged under the following heads :—

1. Combinations and decompositions at ordinary temperatures. 2. Combinations at high temperatures (combustion). 3. Dissolution in liquids. 4. Allotropic and

[1] Sometimes the unit of mass referred to is a kilogram. The corresponding thermal unit may be called a large calorie.

isomeric changes. In the present chapter the first two will be chiefly considered. The others are referred to elsewhere.

A substance in a chemically free or unsaturated condition may be compared to a body which has been raised to a height. In order to get it into such a position, energy in some form must be expended, but the whole of that energy is recoverable in the form of heat or mechanical effect by the descent of the body to its former level. So, when a chemical compound is resolved into its constituents, mechanical work, or rather its equivalent in the form of the kinetic energy of heat or electricity, is transformed into the potential energy of chemical separation; but when the elements come together again in their original order and proportion the same amount of energy is again available, chiefly in the form of heat.

Whenever much heat is evolved, it is tolerably safe to conclude that the resulting compound is a very stable one. Thus when 1 gram of hydrogen combines with $35\frac{1}{2}$ grams of chlorine the result is not only the production of $36\frac{1}{2}$ grams of hydrogen chloride gas, but a certain amount of kinetic energy which becomes manifest in the form of heat. The amount of heat is represented by 22,000 units. In order to reverse this effect, and bring about the decomposition of the compound gas into its constituents, and restore them to their original physical condition, precisely the same amount of energy must be supplied.

All chemical changes which result in the production of more stable from less stable forms of matter, whether by way of combination or of so-called decomposition, are attended by the evolution of heat.

From the following examples it will be seen that, with the thermal values as data, we can predict what will happen if one of the metals is placed in a solution of the chloride of one of the others, which of the oxides is most easily reducible by the action of carbon or other agent, why chlorine decomposes bromides and iodides, and so on.

Heat evolved in the Formation of One Formula-weight in Grams.

Chlorides in Watery Solution.		Hydrated Oxides, Solid.	
$MgCl_2$	186,930	MgO,H_2O	148,960
$ZnCl_2$	112,840	ZnO,H_2O	82,680
$CdCl_2$	96,250	CdO,H_2O	65,680
$HgCl_2$	59,860	—	—
$FeCl_2$	99,950	FeO,H_2O	68,280
$CuCl_2$	62,710	$CuOH_2O$	37,520
$\frac{2}{3}AuCl_3$	18,174	—	—

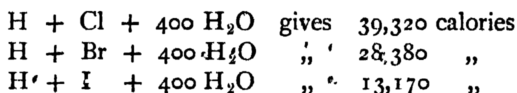
Chlorides.		Bromides.		Iodides.	
KCl	101,170	KBr	90,230	KI	75,020
NaCl	96,510	NaBr	85,580	NaI	70,300
$\frac{1}{2}CaCl_2$	93,820	$\frac{1}{2}CaBr_2$	82,889	$\frac{1}{2}CaI_2$	67,670
HCl	39,320	HBr	28,380	HI	13,170

Suppose, for example, we consider the action of metallic iron on a solution of cupric chloride. The formation of ferrous chloride from iron and chlorine in the presence of water is attended by the evolution of 99,950 calories, while the formation of cupric chloride gives out only 62,710 calories under the same conditions. Hence when iron is introduced into a solution of cupric chloride the one metal will be replaced by the other, while 99,950 − 62,710, or 37,240, calories of heat will be given out.

In general, then, products of chemical combination contain less energy than the materials from which they are formed, the difference being disposed of in the form of heat Such changes are said to be *exothermic*. But in some few cases the reverse is true; that is, the compound contains more energy than its constituents in the state in which they are usually known. Thus the formation of hydrogen iodide, of nitric oxide, of ozone, and probably of acetylene and carbon bisulphide, is attended by absorption of heat,

which is given out if these substances are decomposed. These are said to be *endothermic* compounds.

Comparing together the thermal effects of causing one gram of hydrogen to combine with equivalent quantities of chlorine, bromine, and iodine in presence of water, heat is in each case evolved.



$H + Cl + 400\,H_2O$ gives 39,320 calories
$H + Br + 400\,H_2O$ " 28,380 "
$H + I + 400\,H_2O$ " 13,170 "

A large part of the effect is, however, due to the solution of the resulting hydracids in the water, and if the value of this is subtracted we get a different result.

	Heat of formation in presence of water.		Heat of solution.		Heat of formation of gas.
HCl . .	39,320	—	17,320	=	22,000
HBr . .	28,380	—	19,940	=	8,440
HI . . .	13,170	—	19,210	=	— 6,040

The negative sign means that in production of hydrogen iodide from hydrogen and iodine gases *absorption* of 6,040 units occurs for every unit of hydrogen which combines. The decomposition of hydrogen iodide gas is attended by evolution of heat. We know how prone this compound is to decomposition, and that even a solution of it, provided it is strong, forms a powerful reducing agent, iodine being set free. In very dilute solutions, however, its reducing powers are much less, as may be inferred from the thermal value of its formation in presence of much water.

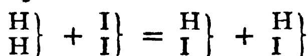
But in such cases as hydriodic acid, after all due allowances have been made for the heat which becomes latent in consequence of the change from solid to liquid, or gas, the actual absorption of heat which is observed must be attributed to the fact that energy is used up in the decomposition of the elementary molecules which precedes, or is simultaneous with, the formation of the molecules of the com-

pound. Thus, when hydrogen combines with iodine, the change is not simply



$$H + I = HI$$

but is, strictly speaking, a double decomposition; thus—



$$\left.\begin{matrix}H\\H\end{matrix}\right\} + \left.\begin{matrix}I\\I\end{matrix}\right\} = \left.\begin{matrix}H\\I\end{matrix}\right\} + \left.\begin{matrix}H\\I\end{matrix}\right\}$$

Now, if the heat required to effect the separation of H from H, and I from I, is greater than the amount of heat generated when 2H combines with 2I, then the result will be negative; no heat will be given out, but a certain amount must be supplied from external sources. From this consideration it is apparent that even in those cases of chemical action in which an evolution of heat is actually observed, this heat represents only the surplus energy remaining over after the breaking up of the molecules of the original substances employed in the experiment.

The estimation of the heat evolved during the neutralisation of an acid by a basic hydroxide is perhaps one of the least difficult of performance, and most intelligible among thermo-chemical measurements. When solution of hydrochloric acid, for example, is mixed with solution of soda sufficient to neutralise it heat is evolved, the amount given out, however, varying to an appreciable extent according to circumstances, whereof the most important are (1) the proportion of water present, and (2) the temperature of the solutions when mixed.

It is obvious, therefore, that the heat produced results from a number of changes, part of which may be physical or mechanical, and part chemical, though in these cases, at any rate, there is no means of distinguishing them. After all, however, the practical object is to compare together the action of substances of the same kind under circumstances as nearly alike as possible.

Thomsen obtained the following values for the heat of

neutralisation of the common acids. This expression means the number of calories evolved when one molecule of a monobasic acid, or an equivalent quantity of polybasic acid, is mixed with one molecule of sodium hydroxide, both being previously dissolved in 100 molecules of water and at the temperature of 16° to 18° C.

Heat of Neutralisation of Acids by Soda.

	Calories.
HCl	13,740
HBr	13,748
HI	13,721
HF	16,272
HNO_3	13,617
H_3PO_2	15,160
HPO_3	14,510
$\frac{1}{2}H_2SO_4$	15,690
$\frac{1}{2}H_3PO_3$	14,228
$\frac{1}{3}H_3PO_4$	11,343
$HCHO_2$	13,450
$HC_2H_3O_2$	13,400
$HC_2H_2ClO_2$	14,280
$HC_2HCl_2O_2$	14,830
$HC_2Cl_3O_2$	13,920
$\frac{1}{2}H_2C_2O_4$	13,840
$\frac{1}{2}H_2C_4H_4O_4$	12,400

It will be noticed that the heat evolved during the neutralisation of these acids does not vary so much as might be expected in view of their diverse composition and character, some, like hydrochloric acid, being reputed strong acids, while some, like acetic acid, are weak acids. So long as the heat of a reaction was supposed to be a measure of the affinities of the substances concerned, such results were difficult to interpret. This idea is, however, now necessarily abandoned, and a clue to the apparent anomaly of a strong

acid and a weak acid producing nearly the same amount of heat in the reaction has been provided by the theory of ionic dissociation. (See Chap. XIX.)

Combustion.– The burning of wood, coal, charcoal, and other matters commonly employed as fuel is a process with which everyone is familiar. Chemists know that the production of fire in the usual way is attended not merely by the consumption or alteration of the fuel, but by changes in the surrounding atmosphere, and that the presence of a sufficient supply of air is an indispensable condition in the operation. They explain the phenomena by stating that the process of burning consists essentially in the combination of the elements of the combustible body with the oxygen in the air, so much heat being developed that more or less of the solid combustible and of the products of combustion are raised to such a temperature that they emit light. Notwithstanding, then, that in ordinary fires the coals disappear and seem to be destroyed, they do in reality only evaporate away in the form of carbon dioxide and water; and if these products could be collected and weighed, their weight would be found to be made up of the united weight of the carbon and hydrogen of the coal, and the oxygen which is taken from the air.

The phenomena of combustion may be observed equally well when other materials are employed. Thus copper burns in vapour of sulphur, hydrogen burns when ignited in chlorine, while phosphorus and several metals become ignited spontaneously when introduced in the proper condition into the same gas. In every such case the resulting product consists of a compound of the body which is burned with one or other of the constituents of the gaseous atmosphere which surrounds it. From this it is evident that the terms 'combustible' and 'supporter of combustion,' as generally employed, involve an error if they are taken to imply any difference of function; for that which in one experiment occupies the position of combustible may be made the

supporter of combustion or atmosphere in another. It is easy to show, for example, that not only will a jet of hydrogen burn in oxygen gas, but that a jet of oxygen burns equally well when surrounded by hydrogen.

Previously to the discovery of oxygen by Priestley, and the establishment of the modern theory of combustion by Lavoisier at the close of the last century, a remarkable theory had been for upwards of fifty years adopted by chemists. This was the celebrated theory of phlogiston,[1] proposed by Stahl.[2] This phlogiston was supposed to be a substance of great tenuity, which, by combining with incombustible bodies, rendered them combustible. When such bodies are burnt, it was imagined that the escape of the phlogiston in a peculiar condition of vibratory motion gave rise to the phenomena of fire. At the time the idea was originally introduced little was known of the part which the air plays in all ordinary burning. When accumulated facts proved conclusively that bodies by burning increase in weight, some attempts were made to prop up the theory by assuming that the presence of phlogiston gave bodies lightness instead of weight. The merit of the idea, however, lay not so much in providing an explanation of certain special cases of combustion, as in referring all cases of burning to a common cause, and in showing that the property of combustibility is capable of being transferred from one body to another. Oxides of the metals, for example, were regarded as ashes, or 'calces,' of the metal left after the escape of their phlogiston, which could be restored to them by contact with heated charcoal, a body which was supposed to be specially rich in the hypothetical inflammatory principle.

While we believe that the presence of no substance such as phlogiston is necessary for the production of fire, and that during the manifestation of the phenomena of combustion no loss of material occurs, yet it has been very

[1] φλογιστός, anything *set on fire*. [2] Died at Berlin, 1734.

justly pointed out that bodies, when they burn, do in truth part with something, and that is the potential energy or power of doing work which belongs to a state of chemical isolation.

In order that combustion may commence in air the temperature of combustible bodies must in general be raised. The temperatures required in different cases are very diverse. Thus phosphorus, which liquefies at 44°, can scarcely be melted in the air without inflammation. Carbon disulphide vapour mixed with air takes fire if a glass rod heated to about 150° is brought into contact with it. Sulphur begins to burn at about 250°—far below its boiling-point; while carbon and many hydrocarbons require a red heat.

The temperature produced when the process of burning is once established is in general higher than that which is requisite for the commencement of combination. This difference is illustrated by the action of platinum upon a mixture of hydrogen or coal gas and air. If a warm slip of clean platinum foil or a coil of platinum wire is held in a current of such mixed gases, the temperature of the metal rises rapidly, in consequence of combination taking place between those portions of the gases which are in immediate contact with it, combination extending to the surrounding mass only when the temperature reaches a certain point, and the platinum is nearly white-hot. Similar phenomena may be observed in other cases when the heat evolved in the early stages of the process is allowed to accumulate. The spontaneous ignition of phosphorus, of finely pulverulent iron or lead (pyrophori), and of heaps of oily rags, may be referred to this cause.

The exact temperature of flame is difficult to determine, and is liable to vary. The temperature of a hydrogen flame, burning in air, has been estimated at about 2080° C., but when the flame is fed with pure oxygen its temperature rises to upwards of 4000° C. This is easily explained by the fact

that in atmospheric air the oxygen is mixed with four times its bulk of nitrogen, which contributes nothing to the chemical action, and which, being raised to the same temperature as the other gases present, consumes a great deal of heat. A temperature still higher is produced when a mixture of hydrogen and oxygen in due proportions is fired in a closed vessel, so that the heated gases are not allowed to expand. This expansion against atmospheric pressure is work the performance of which involves the consumption of heat. The temperature produced by the explosion of oxygen and hydrogen in a closed vessel has been estimated at about 5250° C.

But although the temperatures producible by the same combustible under various circumstances are different, the actual amount of heat evolved in the combustion of the same weight of a given substance is always the same. This statement can of course be accepted only on condition of uniformity in the circumstances attending the experiment. Thus it will appear from the table given below that, as in the case of carbon, the different allotropic modifications of the same substance may give rise to appreciably different amounts of heat.

I. *Units of Heat developed by Combustion of Equal Weights of Elements in Oxygen.*

Substance burned.	Product.	Grams of water heated 1° C. by burning 1 gram or each substance.
Hydrogen	Water	34,034
Carbon—		
a. Diamond	Dioxide	7,770
b. Natural graphite . .	,,	7,797
c. Wood charcoal . .	,,	8,080
Sulphur (native) . . .	,,	2,220
Phosphorus (common) . .	Pentoxide	5,747
Zinc	Oxide	1,330
Iron	Peroxide	1,582

II. *Units of Heat evolved by Combustion of Atomic Weights.*

Name of element.	Weight in grams.	Product.	Grams of water heated 1° C. by the combustion.
Hydrogen . .	1	Water (liquid) . .	34,034
,, ...	1	Hydrogenchloride(gas)	22,000
,, . . .	1	Hydrogenbromide(gas)	8,440
Carbon—			
a. Diamond . .	12	Dioxide (gas) . .	93,240
b. Graphite . .	12	,, ,, .	93,560
c. Charcoal . .	12	,, ,, .	96,960
Sulphur (native) .	32	Dioxide (gas) .	71,042
Phosphorus (common)	31	Pentoxide (solid)	178,157
,, . .	31	Pentachloride (solid)	107,740
Tin	118	Dioxide (solid) . .	135,360
,, ...	118	Tetrachloride (liquid)	122,880

The quantity of heat absolutely evolved also depends partly upon the physical condition of the products of combustion. Thus the number 34,034, which expresses the heat evolved in the combination of one part by weight of hydrogen with eight parts of oxygen, represents not only the heat of chemical action, but the heat (amounting at the temperature of the experiment to about 5,500 units) which is produced by the liquefaction of the resulting nine parts of steam.

This relation of the amount of heat evolved to the physical state of the resulting compounds is further indicated by the results exhibited in the following table :—

Substance burned.	Weight burned.	Product.	Units of heat evolved.
Tin . . .	Sn = 118	SnO_2	135,360
Stannous Oxide .	SnO = 134	SnO_2	69,584 × 2 = 139,168
Copper . .	Cu = 63·5	CuO	38,304
Cuprous Oxide .	$\frac{1}{2}Cu_2O$ = 71·5	CuO	18,304 × 2 = 36,608
Graphite . .	C = 12	CO_2	93,560
Carbonic Oxide .	CO = 28	CO_2	67,284 × 2 = 134,568

Here we find that when solid tin or copper is converted into its highest oxide, the amount of heat developed is practically speaking, twice as great as the amount of heat developed in the conversion of the lower into the higher oxide. In other words, the two successive stages of oxidation, both of which result in the formation of solid products, are marked by the evolution of equal quantities of heat.

The case of carbon is different. In the first stage of oxidation the process involves the conversion of solid carbon into gaseous carbonic oxide, whilst in the second stage the carbonic oxide which is burnt, and the carbon dioxide which is formed, are both gaseous. There is no change of state. Hence the quantity of heat which is developed in the latter operation is nearly two-thirds, instead of only one-half, the total quantity evolved in the formation of the same weight of carbon dioxide from solid carbon.

In order, therefore, to calculate the actual amount of heat obtainable by burning a given combustible it is necessary to take these and other circumstances into consideration. The following examples, which are unencumbered by small corrections, and in which it is assumed that no heat is lost by radiation or conduction, will serve to indicate the general nature of such calculations.

The combustion of 1 part by weight of wood charcoal evolves 8,080 units of heat. That is to say, 1 kilogram of charcoal would heat 8,080 kilos. of water from 0° to 1°, or 1 kilo. of water from 0° to 8080°. 12 kilograms of charcoal produce 44 kilos. of carbon dioxide, or 1 kilo. produces 3·67 kilos.; and if the heat produced by the combustion is communicated to this quantity of carbon dioxide, and not to water, the temperature would be $\frac{8080}{3 \cdot 67}$, or 2202°, if the specific heat of carbon dioxide were the same as that of water. But the specific heat of carbon dioxide is only

·2164 when that of water is 1. Hence the temperature of the carbon dioxide is $2202 \times \frac{1}{\cdot 2164}$, or 10175°, when the carbon is burnt in oxygen.

Now if the combustion is performed in atmospheric air, which contains 77 per cent. of nitrogen, much heat is consumed in raising the temperature of this nitrogen.

The 2·67 parts of oxygen required for the combustion of one part of carbon are accompanied by 8·93 parts of nitrogen, the specific heat of which is ·2438. Therefore, when the combustion of carbon takes place in air, the temperature of the resulting mixture of gases cannot be higher than

$$\frac{8080}{(3{\cdot}67 \times {\cdot}2164) + (8{\cdot}93 \times {\cdot}2438)} = 2720^\circ \text{ C}$$

In practice the temperature is not so high as this, partly because some heat is lost by radiation, some by conduction through the solid unburnt charcoal, partly because an excess of atmospheric air over and above that actually required mingles with the products of combustion, and partly also because the specific heats of the materials employed and of the products formed by their combination are not constant, but increase as the temperature is higher.

A limit is also set upon the temperature produced by any given act of combustion, or generally of chemical combination, by reason of the fact that all high temperature changes are reversible, and sooner or later a point is reached at which the product of union is decomposed. Hydrogen and oxygen, for example, combine to produce water at a red heat, but at the temperature of the electric spark steam is resolved into hydrogen and oxygen, and probably at the latter temperature hydrogen would not burn in oxygen. A spark causes ignition in the mixed gases, because a suitable temperature is provided somewhere in its immediate neighbourhood.

CHAPTER XIX.

ELECTRO-CHEMICAL DECOMPOSITION.

WHEN a plate of zinc is immersed in a solution of hydrochloric acid, hydrogen gas escapes, and the chlorine unites with the zinc, forming a solution of zinc chloride. If now a plate of platinum, which is not acted upon by the acid, is immersed in the same liquid and is made to touch the zinc, or is connected with it by a wire, it will be seen that the hydrogen is no longer disengaged from the zinc plate, but appears on the surface of the platinum in the form of bubbles which rise to the surface of the liquid, while the zinc continues to dissolve as zinc chloride. Such a combination of two metallic plates immersed in a liquid, the action of which on one of them is greater than on the other, constitutes a voltaic cell. A number of these cells joined together forms a battery. A wire connecting the extreme plates of such a series exhibits three chief phenomena. Held lengthwise over a suspended magnetic needle it causes it to be deflected so as to tend to set at right angles to the wire according to a rule which need not be further considered in this place. If the wire is cut in two, that part which proceeds from the zinc can be shown, by a gold-leaf electroscope, to be charged with negative electricity, whilst the wire from the platinum is positive. If these wires are then dipped into a solution of some salt, such as copper sulphate, the elements of the salt are separated, the metal going to the negative electrode or terminal connected with the zinc of the battery, sulphuric acid and oxygen making their appearance at the electrode belonging to the platinum plate[1] of the battery, that is at

[1] The elements which make their appearance at the negative pole are often referred to as *electro-positive*, whilst those which collect at the positive pole are *electro-negative*. The metals are generally electro-positive, the non-metals electro negative.

the positive pole. This process of decomposition by the voltaic current is called 'electrolysis.' It must be remembered that electric currents may be produced by other means in which chemical action is not concerned, as in the dynamo-machine and thermo-electric couples, and hence that chemical and mechanical work are mutually convertible.

Two important quantitative laws relating to electrolysis discovered by Faraday may be expressed as follows: The first states that *the amount of an element, or other substance, liberated is directly proportional to the quantity of electricity flowing through the circuit.* To separate a univalent atom, such as chlorine, from a compound requires a certain fundamental unit of electricity the value of which has been approximately determined. To separate a bivalent atom, such as oxygen, requires twice as much, while a trivalent atom requires three times as much, and so on, multiples of the unit charge being always employed, but never fractions of it.

The second law states that *the elements, or other substances, liberated during electrolysis are set free in the proportion of their chemical equivalents*, and provided disturbing or secondary actions are avoided, these quantities are also chemically equivalent to the materials consumed in each cell of the battery when a voltaic current is used. It will be obvious from the properties of many of the known elements that in certain cases the primary products of the electrolytic process cannot always be collected. This is especially the case when aqueous solutions are used, for such metals as potassium and sodium cannot exist in contact with water, and chlorine under certain circumstances decomposes water, liberating oxygen. If, for example, a solution of potassium chloride is electrolysed, the products actually observed are not potassium and chlorine, but potassium hydroxide and hydrogen at the negative electrode, and hydrogen chloride and oxygen, accompanied by

more or less chlorine, according to the concentration of the solution and strength of the current, at the positive electrode. The quantities of such secondary products are, however, equivalent to the quantities of the primary constituents of the salts employed, and so Faraday's law still holds good.

If, for example, in each cell of a battery 32·5 grams of zinc are dissolved, and the current therefrom passes simultaneously through solutions of potassium iodide, potassium bromide, copper sulphate, silver nitrate, and acidulated water arranged in continuous circuit, the products actually formed in the successive decomposing cells would be as follows:

At the negative or cathode.	At the positive or anode.
1st. H = 1 gram. KHO = 56 grams.	I = 127 grams.
2nd. H = 1 gram. KHO = 56 grams.	Br = 80 grams.
3rd. $\frac{1}{2}$ Cu = 31·75 grams.	$\frac{1}{2}O$ = 8 grams. $\frac{1}{2}H_2SO_4$ = 49 grams.
4th. Ag = 108 grams.	$\frac{1}{2}O$ = 8 grams. HNO_3 = 63 grams.
5th. H = 1 gram.	$\frac{1}{2}O$ = 8 grams.

The constituents of salts which are separated from each other in the process of electrolysis were called, by Faraday, 'ions,'[1] those which go toward the anode or positive plate being called *anions*, while those which travel in the opposite direction toward the cathode or negative plate are called *cathions*.

It is important to distinguish clearly between the ions in

[1] From ἰόν (Gr.) a wanderer.

a compound and the elements when in a free or isolated state. The former are identical with the proximate reacting constituents, which are commonly called the 'radicles of a salt, and are in general coupled together in pairs, or otherwise, when set free from combination. The cathion of an acid, for example, is hydrogen, but this element in the ionic state is not to be confounded with hydrogen gas, which has very different properties. The anions of many salts, such as the sulphates and nitrates, are not known in any separate form. The anion of a sulphate is SO_4, which when separated by electrolysis is at once resolved into SO_3 and O, which appears as oxygen gas.

During the process of electrolytic decomposition the electrolyte is always resolved into its two ions, which make their appearance in the form of the corresponding element or of products of decomposition at the anode and cathode respectively, but observations on the accumulation of these products round the electrodes have led to the discovery that the ions move through the liquid at different rates. Thus in the electrolysis of a solution of hydrogen chloride the hydrogen ion moves towards the cathode more than five times as fast as the chlorine ion towards the anode. This is remarkable if the usual hypothesis is accepted that the passage of a current of electricity is essentially due to the travelling of opposite and equal charges to meet each other, for in such case it would appear at first sight as if there would be inequality of discharge at the surface of the two electrodes and a part of the slower ion left in the liquid. This can only be explained by reference to the views which are now held as to the physical nature of the process of electrolysis.

Before proceeding to give an account of these theories, one or two additional facts should be noted. The products of electrolysis are electrically neutral, and on escaping show no signs of electrical charges such as may be recognised on the electrodes. The ions appear only at the electrodes, and

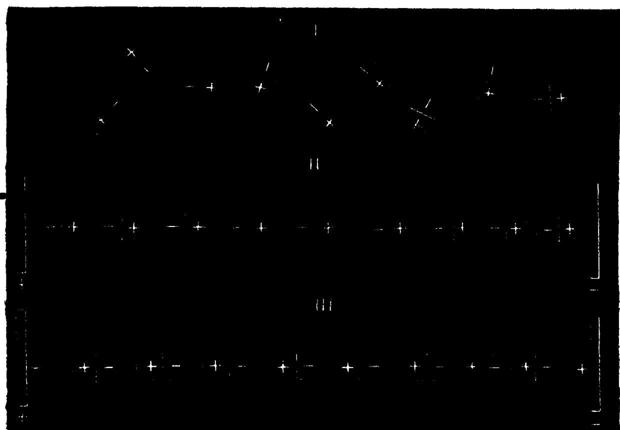
no transit of matter can be detected at any point in the liquid intervening between them.

A hypothesis relating to the mechanism of electrolysis was devised by Grotthus in 1805, and for many years was very generally accepted. In a liquid, such as a solution of hydrochloric acid, each molecule of the electrolyte is supposed to be made up of two parts—one having a charge of positive, the other of negative electricity, in virtue of which these constituents are united together. According to this hypothesis, then, chemical affinity is nothing but the attraction of oppositely electrified particles. When a current is sent through such a liquid, the first effect is the establishment of a great number of chains of molecules in which the positive elements all face in one direction, the negative elements in the other. Then the metal plates at different potentials which form the electrodes attract the atoms of opposite electric name from the two ends of the polar chains, and detach them from the state of chemical combination in which they previously existed.

The following diagrams serve to illustrate the successive conditions supposed to prevail in the liquid. In the first the molecules of the electrolyte are moving about in the liquid mass in every direction. Then these molecules arrange themselves into chains in the order shown in II, and in III the disruption of the end molecules occurs, and is followed by a change of partners throughout the length of the chain. Thus the disengagement of hydrogen at the negative electrode, and of an equivalent quantity of chlorine at the positive, without any apparent change in the intervening mass of liquid, is accounted for.

This hypothesis is now generally regarded as insufficient. It has long been known that the very smallest electromotive force is sufficient to make a current of electricity pass through a saline solution, from which it appears that the two ions of a salt are not held together by any force, and that they are probably separate before the current is

applied. The fact is also recognised that, in general, electrolytes are the only compounds which enter readily into the chemical process of double decomposition, which is the characteristic of the class of compounds called *salts*. As already explained (p. 19 and elsewhere), there are good reasons for believing that the molecules of liquids and gases subsist unceasingly in a state of motion. Their agitation is increased by heat, diminished by cold. In the course of this dance in which they are engaged, and the



numerous encounters which must occur among them, it is conceivable that some of the molecules get broken up into atoms or atomic groups, which for a while wander about until they encounter some other atom or atomic group with which they can unite. If the original body was homogeneous, the molecules which are thus reproduced are of the same kind as the original molecules. So long as this work of reproduction goes on at the same rate as the destruction—that is, so long as, in a given interval, the number of molecules decomposed and the number of molecules recomposed

is the same—no change occurs in the properties of the body, because the average composition of the mass remains the same. In a mass of hydrogen chloride gas, for example, it is conceived that if it were possible to submit it to such a scrutiny, the greater part of the mass taken at any instant would be found to consist of molecules, each made up of an atom of hydrogen and an atom of chlorine; but that with these there would be associated a certain number of free atoms of hydrogen and chlorine interspersed among them. In the next instant many of these free atoms would be seen yoked together again, whilst their places would be supplied by the disruption of fresh molecules. This hypothesis was introduced by Williamson about fifty years ago.

A similar condition is supposed to prevail in a liquid, and the action of the current is merely to direct the already separated atoms to the opposite electrodes. Thus an atom of hydrogen being within a certain distance of the positive electrode may be supposed to receive a charge of positive electricity, the possession of which causes it to be attracted to the surface of the negative electrode, where it arrives in company with other atoms similarly charged. On reaching the electrode the atoms give up their charges to it, and then pair off to form molecules.

Within the last few years this hypothesis, which we owe to Clausius, has undergone an important modification at the hands of Professor Arrhenius. It is now believed that liquid electrolytes are in a state of dissociation more or less *complete* before they are acted upon by the current, and that the current passes through the liquid wholly by means of the free ions which transport specific quantities of electricity corresponding to their valencies. The substances which are most easily decomposed by the current are the substances known as acids, bases, and salts, and their chemical activity seems to depend upon the extent to which the ions have been dissociated. It has been shown by direct experiment that solutions of various acids stand in the same order in

regard to electric conductivity and in regard to their power of effecting chemical changes, such as hydrolysis of sugar or other substances. A 'strong' acid is therefore now understood to be one which is more completely dissociated into its ions than a 'weak' acid.

It will be noticed that the terms 'dissociate' and 'dissociation' are used in a sense different from their application to the phenomena produced by heat. Water is said to dissociate at high temperatures into hydrogen and oxygen, and these two elements in the gaseous form may actually be separated by the process of diffusion. No appreciable diffusion of ions, however, has been observed, and no means are yet known whereby one ion can be removed from near association with its opposite partner.

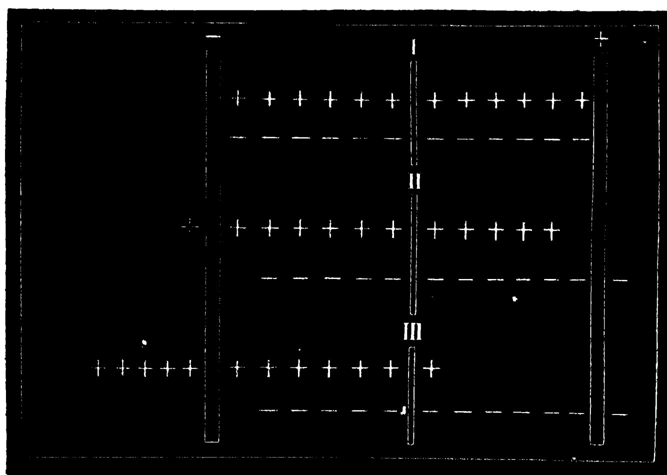
The following diagram will assist in the conception of this idea, and may be compared with the previous diagram which was employed to illustrate the hypothesis of Grotthus :—



Here there are but few complete molecules in a liquid such as dilute sulphuric or hydrochloric acid or any other good conductor, while the ions are represented as more or less independent of one another. The extent of their freedom and the part played by the liquid in which they move are, however, matters upon which considerable difference of

opinion still exists. According to this hypothesis the negative ions all move with their charges in one direction, while the positive ions go with their charges in the opposite direction, and the complicated rearrangements required by the Grotthus theory are not called for.

It will be easy now to explain how it comes about that notwithstanding the fact that the number of positive and negative units discharged is always the same, the concentration of the liquid round the two electrodes gradually changes owing to the difference in the rates of movement of the ions through the solution. By making use of a cell divided by a porous partition to prevent mechanical intermixture of the liquids round the electrodes, the difference of concentration after electrolysis has proceeded some time can be easily measured. In the following diagram I. may be supposed



to represent the condition of either II. or III. previously to electrolysis. On each side of the central division there are materials of six molecules. Each + and − without a partner represents an ion discharged. After the passage of

the current in II., which stands for potassium chloride, the number of molecules of chloride on each side will be reduced from six to five, but the concentration, though lessened on both sides, remains equal, because the K ion moves at nearly the same rate as the Cl ion. The case represented by III. is that of hydrogen chloride. Here the H ion moves about five times as fast as the Cl ion, and consequently of the six molecules which remain undecomposed the materials of five are found on the left, while there is only one on the right of the partition, six atoms of hydrogen and six atoms of chlorine having been eliminated.

The electrolytic conductivity of a given liquid depends partly upon the number of ions available for the passage of the current and partly on the rate at which they move. There are, however, many phenomena connected with electrolysis which are still very obscure. Liquid carbon dioxide, cyanogen, carbon bisulphide, hydrogen chloride, and stannic chloride, when perfectly free from water, do not conduct and are not decomposed, and the conductivity of water itself is so small that its determination has been a matter of special difficulty.

On the other hand, certain salts, such as the chlorides and iodides of lithium, calcium, barium, lead, and silver, when melted, conduct readily and are easily electrolysed. It is not easy to see in what respect melted silver chloride, for example, differs from hydrogen chloride or stannic chloride, which are liquid at common temperatures. Yet we must suppose that silver chloride and the rest are partially ionised by the process of fusion, although the temperature, in the case of silver chloride at any rate, is far below a red heat.

Although anhydrous hydrogen chloride and tin chloride are non-electrolytes the case is different if water is added. Such solutions are electrolysed very readily, and the products which result primarily consist of the ions of the dissolved substance. No other liquid is known which possesses

in the same degree as water the power of setting up the state of ionic dissociation in a dissolved salt.

It has been found by experiment that the molecular conductivity of an acid or a salt is increased by dilution. In the case of good conductors a limit is soon reached, but in bad conductors the molecular conductivity goes on increasing indefinitely till the liquid is too dilute for measurement, and the influence of slight impurities in the solution becomes appreciable.

The following table shows the relative molecular conductivities of equivalent solutions of a few acids, bases, and salts, at the temperature of 18°, from the results of experiments by Kohlrausch. The unit employed is the resistance of the mercury unit of Siemens, that is, a column of mercury one metre long and one square m.m. in section. The reciprocals of the numbers obtained represent the conductivities.

1 gram molecules in	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	$HC_2H_3O_2$
1 litre	278	277	189	1·2
10 litres	324	323	208	4·3
100 "	342	340	286	13·2
1000 "	346	343	332	38·0

	KHO	$NaHO$	NH_4HO
1 litre	172	149	0·84
10 litres	199	170	3·1
100 "	212	187	9·2
1000 "	214	188	26·0

	KCl	$NaCl$	$\frac{1}{2}BaCl_2$	$\frac{1}{2}MgSO_4$
1 litre	92	70	66	27
10 litres	105	87	86	47
100 "	115	96	101	72
1000 "	119	101	109	94
10000 "	121	103	113	103

From these examples it will be seen that the conductivity of each substance increases with the addition of water to the solution, but that the increase of conductivity is less as the dilution proceeds, and it tends towards a limit, that is, it reaches a value which is not increased by further dilution. The substances of weak conductivity are affected proportionally much more than substances which are good conductors. For example, while the conductivity of hydrogen chloride is increased by dilution from 1 litre to 1,000 litres in the ratio of 1 to 1·24, the conductivity of sulphuric acid is raised in the proportion of 1 to 1·75, while that of acetic acid is increased from 1 to 31. It will also be noticed that the conductivities of potassium chloride and sodium chloride, each of which consists of two univalent ions, are increased to a small extent as compared with magnesium sulphate, which is composed of two bivalent ions. Molecular conductivity appears to depend, as already stated, upon the number of ions present, that is on the extent of dissociation of the compound, together with the velocities of the dissociated ions. The difference then between a strong acid and a weak acid is accounted for by the hypothesis that the strong acids and other relatively active substances owe their chemical characters as well as their conductivity to the greater extent of their dissociation, so that dilution has a relatively small effect on them, while it causes a rapid increase in the state of dissociation in weak acids and other compounds which are comparatively feeble as reagents.

As the molecular conductivity of a solution by successive dilution increases up to a limit, this value may be regarded as equal to the conductivity at infinite dilution.

Every solution of an electrolyte must therefore be thought of as a mixture of the solvent with molecules of the dissolved substance, and with the ions into which a certain number of the molecules are resolved. According to the hypothesis the extent of ionisation determines the conductivity and the chemical activity of the substance.

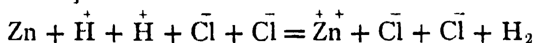
When the dissociation is complete, as it may be supposed to be in a solution infinitely diluted, the conductivity reaches a maximum, but in all other less dilute solutions the conductivity per molecule is less. The question how many of the total number of molecules present are dissociated into ions is not answered by direct appeal to the conductivity, but is determined by the ratio between the conductivity of the solution to the conductivity of the same when infinitely diluted. It is usually expressed as follows, denoting by μ_v the conductivity of the solution when v is the volume in litres containing one gram-molecule of the substance, and μ_∞ the conductivity when v is infinitely great, then m, the dissociation, is found by the equation

$$m = \frac{\mu_v}{\mu_\infty}.$$

As m represents the proportion of the dissolved substance which exists in the form of ions, $1-m$ is the proportion which exists in the form of molecules. It has been shown by Ostwald that $\frac{m^2}{(1-m)v}$ is a constant. This is usually indicated by k, and is called the dissociation constant. Its value is dependent on the nature of the dissolved substance, and is the same for all dilutions.

A few examples may now be given of the application of the dissociation hypothesis to some familiar chemical changes. Since a solution of an acid is supposed to contain the ions of the acid associated with positive and negative charges of electricity respectively, and the solution of a salt similarly contains the ions of the salt, the dissolution of a metal in an acid with evolution of hydrogen gas involves the change of ionic hydrogen into molecular hydrogen, and of molecular metal into ionic metal. The solution of zinc, for example, in diluted hydrochloric acid is due to the transfer of two positive changes from the

hydrogen ions to the zinc. The equation then might be written

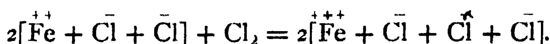


$$Zn + \overset{+}{H} + \overset{+}{H} + \overset{-}{Cl} + \overset{-}{Cl} = \overset{++}{Zn} + \overset{-}{Cl} + \overset{-}{Cl} + H_2$$

On comparing together the behaviour of different metals in regard to water and acids under different conditions, it becomes obvious that the various effects may be attributed partly to certain inherent peculiarities of each metal, which in the present state of knowledge cannot be further explained, and partly to the conditions which favour contact between the metals and the ions assumed to be present in the liquid. Water is believed to contain very few ions, and the violence with which the liquid is attacked by sodium must be due to some peculiarity of the metallic atom in this case, in consequence of which it takes up the charge from the hydrogen very readily. On the other hand, copper, tin, or zinc is incapable of being ionised by liquid water, and even by hydrogen chloride copper and tin are, under ordinary circumstances, ionised very slowly. A stream of the ions in such liquid, produced either by contact with a less active metal, such as platinum under the surface of the liquid, or by means of a current of electricity directed through the metal and the liquid, causes rapid ionisation of the metal.

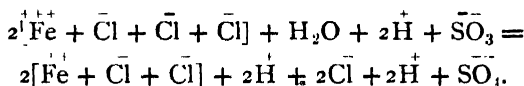
This recalls the fact that the valency of many elements is capable of being changed, and, if the ionic doctrine is accepted, this must be due to a change in the number of unit charges of electricity which the atom is made to carry. The conversion of a ferrous into a ferric salt is thus due to a change of the ferrous ion $\overset{++}{Fe}$ into the ferric ion $\overset{+++}{Fe}$. The process known as 'oxidation' implies, not necessarily the employment of oxygen, but the use of some agent whereby equal positive and negative charges are produced. In an aqueous solution of ferrous chloride mixed with hydrogen chloride it is probable that the greater part of these com-

pounds is dissociated. The addition of chlorine, which is electrically neutral, gives rise to additional chlorine ions each with a negative charge, which arouses a corresponding positive charge on the metallic ion. The equation would be expressed as follows:—



$$2[\overset{++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl}] + Cl_2 = 2[\overset{+++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl} + \overset{-}{Cl}].$$

On the other hand, ferric compounds are converted into ferrous by the action of a variety of reagents, and the process is known as 'reduction.' Ferric chloride, for example, is converted into ferrous chloride by the action of sulphurous acid. In this case we must suppose that the conversion of the sulphurous ion into sulphuric is accomplished with the aid of oxygen derived from water, the hydrogen of which becomes ionised at the same time. The change would probably be represented by the following equation, supposing that all the substances present except water are completely dissociated:—



$$2[\overset{+++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl} + \overset{-}{Cl}] + H_2O + 2\overset{+}{H} + \overset{--}{SO_3} =$$
$$2[\overset{++}{Fe} + \overset{-}{Cl} + \overset{-}{Cl}] + 2\overset{+}{H} + 2\overset{-}{Cl} + 2\overset{+}{H} + \overset{--}{SO_4}.$$

On the hypothesis that electrolytes are dissociated into their ions more or less completely when dissolved in water, it is obvious that solutions containing the same ion in equal quantities ought to exhibit uniform properties provided the associated ion does not interfere. For example, solutions of copper nitrate, sulphate, chloride, and acetate contain the copper ion, and accordingly they exhibit the same blue colour when sufficiently diluted. Similarly, the soluble salts of lead, of mercury, of silver are colourless unless the metal is associated with a negative ion, such as that of the chromates, which possesses a colour of its own. It will be noticed that it is only when the salt is in solution and in a

state of dissociation that this is true. Such a salt as lead iodide, which is yellow when in the solid form, is no exception, for the solution of this compound in water is perfectly colourless. Mercuric iodide, again, has a scarlet or yellow colour when solid, but though it is not soluble in water it dissolves in common ether or in solution of potassium iodide, and the solutions are perfectly colourless.

In some cases marked changes of colour are produced by altering the concentration of a solution of a coloured salt. For example, a strong solution of cupric bromide is deep brown, but on adding water it becomes blue; cobaltous chloride in the solid state and in concentrated solution is deep blue, but in dilute solutions it is red. Such changes of colour have hitherto been explained by assuming the existence of several hydrates containing the elements of the salt associated with different proportions of water of crystallisation. The ionic hypothesis supposes that concentrated solutions contain a certain number of molecules of the salt undissociated, and these molecules may exhibit different colours and other properties. When sufficiently diluted it is assumed that in each case the ions are more or less completely separated, and each produces its effect independently. We know that in dilute solutions the influence of electrolytes upon the freezing point, the boiling point, and the osmotic pressure, is approximately twice as great as that of non-electrolytes. In the case of cobalt chloride the salt is known in the form of blue anhydrous crystals, and also combined with $2H_2O$ or $6H_2O$, forming crystals which are red and nearly of the same tint as the solution. So that even in the solid state it would appear that a certain degree of ionisation may exist. In solution the extent of dissociation may be reduced, as in the case of thermal dissociation, by increasing the proportion of one of the products of dissociation. If a soluble chloride, such as hydrogen chloride or sodium chloride, is added in sufficient quantity to a red solution of cobalt chloride, the colour

tends to blue in consequence of the reproduction of molecules of cobalt chloride and disappearance of part of the cobalt from the ionic form.

The process of neutralising an acid by a basic hydroxide has been already partly explained. It was pointed out (p. 306) that when an acid is neutralised the heat generated in the process varies much less than might be expected in view of the diverse characters of the acids. From the list given we may select those which give very nearly the same amount of heat when neutralised by soda, and we see that they are the strong acids which by direct experiment are shown to be the best conductors and are probably most completely dissociated.

HCl	13740
HBr	13748
HI	13721
HNO_3	13617
$\frac{1}{2}H_2C_2O_4$	13840

The explanation of higher or lower values is derived from two considerations. The weaker acids are believed to be dissociated to a smaller extent than the stronger acids, that is to say, an appreciable portion exists in the solution in the molecular state. Consequently less heat is evolved because the heat produced by the formation of the water is diminished by the heat necessary to break up the acid into its ions. The decomposing or hydrolytic action of water on the salt produced is another cause of irregularity, the amount of heat being thereby reduced, because a smaller number of the hydrogen and hydroxyl ions unite to form water.

The chemical differences between the fixed alkalis and solution of ammonia are also accounted for in an interesting way by the ionic hypothesis. A solution of ammonia contains the greater part of the ammonia in the molecular form of NH_3. This substance by itself accounts for the production of amides on the addition of solution of

ammonia to various salts, such as those of mercury or such esters as ethyl oxalate, also the formation of a great variety of addition compounds like those produced by copper salts. But it probably takes no direct part in the reactions which result in the precipitation of metallic hydroxides. These changes must be attributed to the small quantity of ammonium hydroxide NH_4HO which must be assumed to exist in the solution, and of that only to the portion which is ionised. How very small an amount of dissociated substance is present is suggested by comparison of the molecular conductivity of solutions of ammonia with that of solution of potash or soda (p. 324), and how comparatively feeble is the alkaline character of aqueous ammonia is shown in a variety of ways. Added to solution of calcium chloride, for example, it produces no precipitate, although calcium hydroxide is but slightly soluble, and although a precipitate is produced in a magnesium solution, the hydroxide is not thrown down if a small quantity of ammonium chloride is previously added. The number of ammonium ions being increased by the presence of the ammonium salt, the dissociation of the ammonium hydroxide is so diminished that it is incapable of reacting with magnesium compounds in solution.

CHAPTER XX.

SOLUTION.

BEFORE proceeding to theoretical matters a brief review of the principal phenomena connected with the act of dissolution of a solid in a liquid and the properties of the resulting solution will be useful.

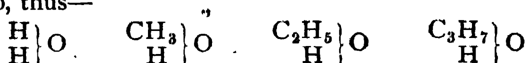
1. Considering any solid chosen as an example, we find that it is not soluble in all liquids. For example, common salt is readily and abundantly soluble in water, to a smaller

extent in alcohol, and not at all in oils. On the other hand no liquid is capable of taking up every kind of solid. Water dissolves sugar, common salt, nitre, and saline substances generally, but it has no appreciable solvent action upon many common metals and minerals, such as iron or copper, limestone or quartz, neither does it dissolve fat, oil, or hydrocarbons generally.

Again, alcohol dissolves many carbonaceous substances, such as resins, phenols, acids, which are almost unaffected by water. Ether and benzene dissolve freely fats and solid hydrocarbons. Carbon bisulphide, which dissolves no salts, takes up many carbonaceous substances, and is the best solvent for common sulphur. Phosphorus trichloride and tribromide dissolve phosphorus. Fluid mercury dissolves many metals, but no other kind of substance.

There seems to be little doubt, in fact, that solubility is often dependent in some degree upon the existence of a similarity in composition between a solvent and the solid it dissolves. *Similia similibus solvuntur.* This is further illustrated as follows :—

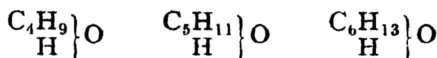
Salts which contain water of crystallisation are, with comparatively few exceptions, easily soluble in water. Such compounds may be regarded as closely resembling water itself. A molecule such as $MgSO_4\ 7H_2O$ may, in fact, be considered as a congeries of eight water molecules, in which one molecule of water is replaced by the elements of the salt. Again, the lower terms of the various series of alcohols and carbon acids show considerable similarity to water in their general behaviour, the higher terms much less. The lower terms of a series like the ethylic series of alcohols may be regarded as consisting of the elements of water, having one atom of hydrogen replaced by a hydrocarbon group, thus—



$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O$$

These are miscible with water in all proportions. But when

the hydrocarbon radicle becomes larger and more complicated, the resemblance to water and the miscibility with water is less. Thus—



$$\left.\begin{matrix}C_4H_9\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}O$$

are compounds of the same series as the foregoing, but they are not capable of mixing with water save in limited quantity. On reaching the highest known terms of the same series, we find waxy solids which are insoluble in water, but dissolve easily in ether or in hydrocarbon liquids, and themselves bear a strong resemblance to solid paraffin. The alcohol, $C_{16}H_{33}HO$, may be regarded as formed of the elements of the hydrocarbon, $C_{16}H_{34}$, in which H is replaced by HO, the latter, however, forming a very small proportion of the entire molecule. In the following series of compounds it will be noticed that the solubility in water increases as the amount of water residue, HO, present in the molecule increases.

Name and Formula.		Solubility in Water.
Benzene	C_6H_6 . . .	insoluble.
Phenol	$C_6H_5(HO)$ . .	slightly soluble.
Catechol, Quinol, Resorcinol	$C_6H_4(HO)$ . .	easily soluble.
Pyrogallol	$C_6H_3(HO)_3$ . .	still more soluble.

The solubility of the majority of substances in any given liquid is usually limited, and varies with the temperature. A few examples will be given further on (3).

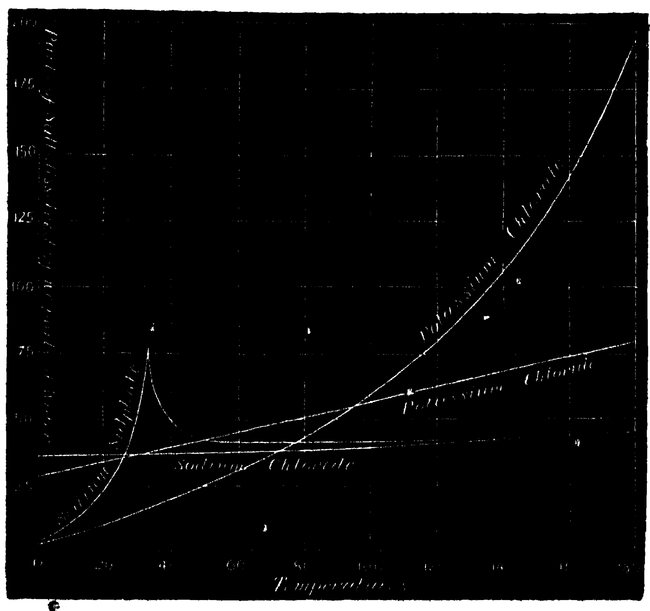
2. The fusibility of a substance has much to do with its solubility. Thus, in comparing together three such very similar salts as chloride, bromide, and iodide of potassium, it is found that at all observed temperatures the most fusible, namely, the iodide, m.p. 634°, is more soluble in water than the bromide, m.p. 699°, and this again is more soluble than the chloride, m.p. 734°. However, it by no means follows that fusibility alone confers the property of solubility,

for while sodium chloride dissolves abundantly in water, silver chloride, though much more easily fusible, is insoluble. The effect of fusibility is best observed when pairs of substances which are both soluble to some extent in a given menstruum are compared together at various temperatures.

3. This leads to another relation very generally observed, namely, that the solubility of solids usually increases with rise of temperature ; in other words, a hot liquid dissolves a given solid more freely than the same when cold. Thus 100 parts of water dissolve—

Of	KNO_3	KCl	$KClO_3$	$NaCl$
At 0°	13·3	29·2	3·3	35·7
At 100°	247·0	56·5	56·5	39·8

These relations are best exhibited graphically in the following manner.



Here the divisions on the horizontal line represent temperatures, whilst those on the vertical express parts of salt dissolved at the several temperatures in 100 parts of water.

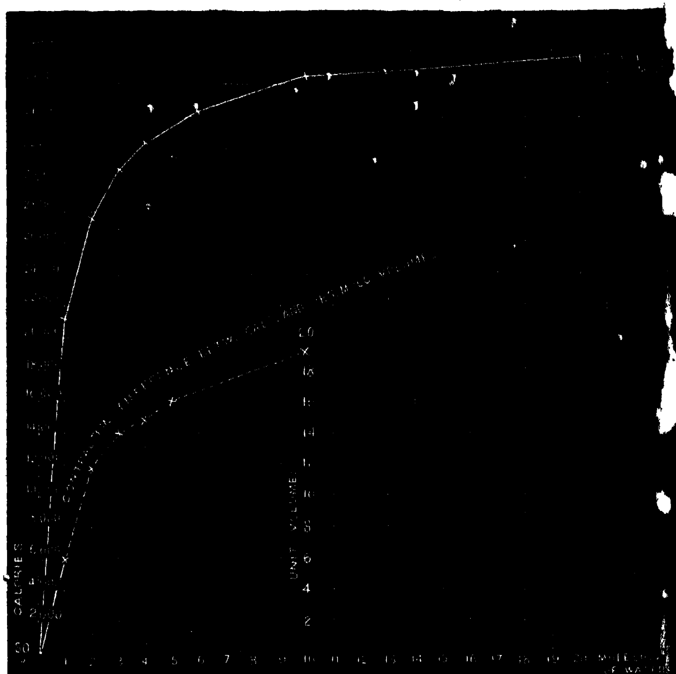
It will be noticed that the solubility of the easily fusible chlorate (m.p. 359°) increases rapidly with rise of temperature, whilst, on the other hand, the potassium chloride (m.p. 734°) and sodium chloride (m.p. 772°), which melt at higher temperatures, exhibit only a slight increase of solubility under the same circumstances.

To the rule that solubility increases with rise of temperature there are many apparent exceptions. Thus lime, calcium sulphate, and sodium sulphate are partly precipitated when a solution of each, saturated in the cold, is heated to boiling. In every case of this kind, however, there is no real anomaly, for the substance deposited always differs in composition from the substance dissolved; thus the crystals which fall when a saturated solution of sodium sulphate is heated are anhydrous, whereas the crystals deposited at temperatures below 33° contain $10H_2O$.

4. When a solid dissolves in a liquid there is always a rise or a fall of temperature in the mass. Moreover, when the solution thus formed is mixed with more water there is again evolution or absorption of heat. The fall of temperature observed when such solids as common salt or nitre are dissolved in water is merely due to the change from the solid to the liquid state. Many freezing mixtures, as of salt and snow, or sodium sulphate and strong hydrochloric acid, act by liquefying. On the other hand, when dry calcium chloride or sodium sulphate, or sodium carbonate dissolves in water, heat is produced, some of which, at least, is due to the chemical combination of the salt with a portion of the water.

In the following diagram is represented the thermal effect of adding successive doses of water in molecular proportions to sulphur trioxide. The calorie is an amount

of heat sufficient to raise the temperature of one part of water one degree. The divisions of the horizontal lines represent the number of water molecules added, and those on the vertical show the amount of heat evolved at any one stage, or in the entire process.



It will be seen that the thermal change becomes less and less as the liquid is diluted, tending continually towards the limit which is represented by the horizontal line.

5. In the act of solution of solids, and especially of anhydrous salts in water, the volume of the solution is always less than the sum of the volumes of the solid and

its solvent, with the exception of some ammonium salts, in which case it is greater. Similarly, the addition of water to a solution is followed by contraction.

The diagram already given exhibits the amount of contraction observed in the case of sulphuric acid and water, and the following table shows the observed and calculated molecular volumes by which the amountof contraction is indicated:

n	Molecular Volumes of $SO_3 + nH_2O$.		Contraction = Difference between calculated and observed Mol. Vol.
	Density.	Mol. Vol. = $\frac{\text{Mol. Wt.}}{\text{Density}}$	
0	1·940 (Solid.)	41·23	—
1	1·842	53·20	6·03
2	1·774	65·39	11·84
3	1·652	81·11	14·12
4	1·547	98·25	14·98
5	1·475	115·25	15·98
10	1·286	202·18	19·05

The contraction consequent on the first addition is greater than the second, and for each succeeding molecule is a diminishing quantity, becoming rather less than 1 after addition of $3H_2O$.

A similar result ensues if we calculate the contraction following upon the dilution of liquid H_2SO_4 with successive quantities of water.

The explanation of this contraction is unknown; the change of temperature always observed is partly due to the contraction. In both cases the effect is produced, not *per saltum*, but continuously, though in gradually decreasing amount as the water is added.

6. When a solid is dissolved in a volatile liquid the evaporation of the liquid is impeded, the pressure of the escaping vapour is reduced, and the boiling point of the liquid is raised.

The table which follows shows the effect of adding common salt to water.

Pressures of vapour evolved from pure water, and reduction of pressure on adding n molecules of NaCl to 100 H_2O at temperatures t°.

$t^\circ =$	70°	75°	80°	85°	90°	95°
	mm.	mm.	mm.	mm.	mm.	mm.
Water	233·3	288·8	354·9	433·2	525·5	633·7
$n = 2$	8·5	10·8	13·7	16·4	20·4	24·6
$n = 4$	18·0	22·5	28·0	33·8	40·9	50·2
$n = 5$	22·6	28·5	35·2	43·0	52·5	63·3

A saturated solution of common salt under the pressure of one atmosphere boils at 108·4°.

It is now known that so long as the solutions used are not very strong the effect produced in lowering the vapour pressure, or in raising the boiling point, is directly proportional to the amount of substance dissolved, and different substances which by solution undergo no chemical change produce the same effect when used in the proportion of their molecular weights.

This is the basis of a method for determining molecular weights already described (p. 90).

7. It has long been known that salt water does not freeze so easily as fresh water, and in general the addition of any substance to a liquid in which it can dissolve lowers the freezing point of the liquid. A solution of 1 part of sodium chloride, for example, in 100 parts of water freezes at about 0·6° below the freezing point of pure water, and a strong brine will remain liquid at about 20° below the ordinary freezing point. When such a solution is made to freeze the crystals which separate at first consist of the pure solvent. After a certain concentration is reached mixtures are deposited from which neither salt nor ice can be separated, and which melt and solidify like a homogeneous mass. Such mixtures are called cryohydrates.

The following are some examples :—

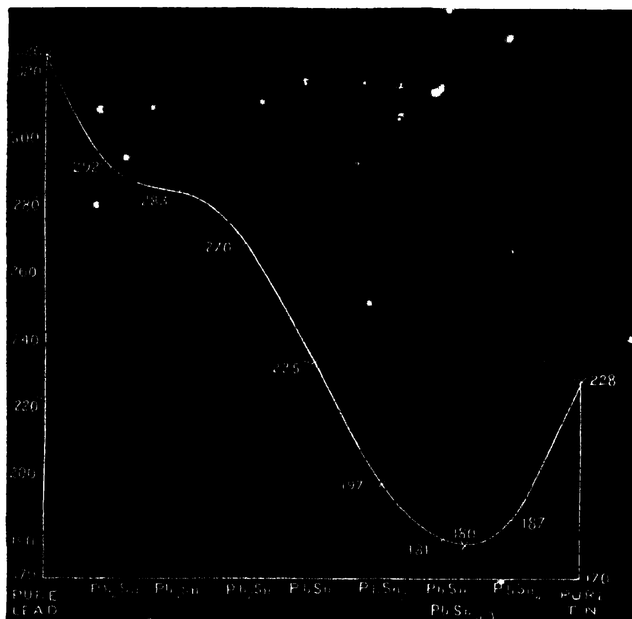
Cryohydrate.		Temperature of Solidification.
$ZnSO_4 + 20H_2O$	approx.	$-7°$
$MgSO_4 + 24H_2O$	,, ...	$-6°$
$KNO_3 + 44H_2O$	,, ...	$-2{\cdot}7°$
$K_2Cr_2O_7 + 292H_2O$	,, ...	$-1°$

Similar facts are observed in connection with alloys. When one metal is dissolved in another in a liquid state, and the whole is allowed slowly to cool, the first deposited solid consists of crystals of the metal which is in greatest amount and which may be regarded as the solvent, the other remaining in the mother liquid till a certain degree of concentration is reached, and the whole then solidifies at a definite temperature. On this principle is based the well-known process for the concentration of silver in argentiferous lead.

In many other cases a mixture of two or more substances melts at a lower temperature than either of the ingredients. Mixtures of the fatty and other acids melt at lower temperatures than the pure acids ; the carbonates of potassium and sodium melt more easily when mixed than when alone ; an alloy of potassium and sodium is liquid at the ordinary temperature ; and an alloy of cadmium, tin, lead, and bismuth melts in hot water.

The diagram on the next page represents the melting points of lead and tin and various mixtures of the same. It will be noticed that while the melting point of tin is 228°, the temperature of liquefaction is lowered to 187° by mixing four atoms of tin with one atom of lead, although the melting point of the latter is considerably above that of tin —namely, at 326°. And upon trial it is found that if lead and tin are mixed together in the proportions of very nearly 2 parts of tin to 1 part of lead, or 3·3 atoms of tin to 1 atom of lead, the melting point is reduced to 180°, and no alloy

containing the same metals in any other proportion melts at a lower temperature. This sort of mixture of minimum melting point has been called a eutectic mixture, and the phenomenon has been called 'eutexia.'



Blagden, in 1788, found that the depression of the freezing point is proportional to the amount of dissolved substance, and Raoult, in 1883, established the law that in dilute solutions molecular proportions of different substances of the same chemical character lower the freezing point to the same extent. This has already been referred to as the basis of a method of determining molecular weight (see p. 89).

18. An aqueous solution of sugar or of salt is heavier than

water, and may be readily poured through a funnel with a long stem into a glass of water in such a way as to form a separate stratum at the bottom. If the solution is coloured it will soon be noticed that the colour gradually extends upwards through the liquid, until after a few hours or a few days, according to circumstances, the whole liquid is tinged. But it is not necessary that the liquid should be coloured. The taste, specific gravity, refractive power, or the application of chemical tests will soon give indications that the solution from below is mixing with the liquid above. This process of spontaneous intermixture or diffusion results from the proper motion of the molecules of the liquid.

The power of interdiffusion is by no means universal among liquids, some liquids being, like mercury, oil, and water, quite incapable of mixing together under any circumstances; while others, such as water and solution of hydrochloric acid, mingle rapidly. We are indebted for nearly all the information we possess on this subject to the late Professor Graham. His experiments were conducted very nearly in the manner just described. The glass vessel in which diffusion was allowed to go on was graduated into equal divisions, from the bottom upwards; and after the introduction of the two liquids the whole was left in a room, the temperature of which was kept as uniform as possible. After a time, the liquid occupying successive divisions of the vessel was removed by a small syphon or pipette and analysed, in order to ascertain the extent to which diffusion had taken place. In this way a number of conclusions were arrived at, among which the following are the most important:—

a. Bodies are divisible, as regards their diffusive power, into two classes. Those which diffuse most readily through a given liquid menstruum are, for the most part, crystallisable substances, and were termed by Graham *crystalloids*; while the least diffusible bodies are uncrystallisable, with, in most cases, high molecular weight, and are denominated

colloids,[1] from their resemblance to glue, which may be taken as the type of this class. The following list supplies the *times* of equal diffusion by the substances there named ; and it will be seen that albumen and caramel, both of which are uncrystallisable substances of somewhat indefinite composition, are far behind the rest :—

Hydrogen chloride	1
Sodium chloride	2·33
Sugar	7
Magnesium sulphate	7
Albumen	49
Caramel	98

Thus hydrogen chloride diffuses more than twice as rapidly as sodium chloride, seven times as rapidly as sugar or magnesium sulphate, forty-nine times as rapidly as albumen, and nearly one hundred times as rapidly as caramel. Hydrogen chloride is one of the most diffusive substances known.

b. Equal rates of diffusion are exhibited in many cases by the members of isomorphous groups. Thus hydrochloric, hydrobromic, and hydriodic acids have nearly the same diffusion rate ; so also have the chlorides, bromides, and iodides of the alkali metal ; the nitrates of barium, strontium, and calcium, and the sulphates of magnesium and zinc.

c. The rate of diffusion increases with the temperature, and when the solution is not too concentrated is proportional to the strength of the solution.

By taking advantage of this difference in diffusibility mixed salts may be separated from one another to a certain extent, and crystalloids may be isolated pretty perfectly from admixture with colloids. In the practical application of this process it has been found convenient to separate the

[1] κόλλα, glue.

liquids undergoing diffusion by some membrane or partition composed of colloid material, and this mode of diffusion, through a septum, is called *dialysis*. The process is a very simple one. The liquid holding in solution a mixture of crystalloids and colloids is placed in a bag or tray of parchment paper, which is suspended in a dish of pure water, which after a time can be renewed if necessary. Under these circumstances the crystalloids pass out by diffusion through the membrane (which must be perfectly free from holes), and by evaporating the liquid down may be obtained in a condition of tolerable purity.

The application of this method led to the discovery of the soluble colloidal forms of ferric hydroxide, silicic acid, alumina, which had been previously known only in the insoluble gelatinoid condition. If, for example, we take a solution of silicate of sodium, and add to it a slight excess of hydrochloric acid, we obtain a perfectly clear liquid, which contains the very substance referred to above as colloid silicic acid; but in this liquid it is mixed with the acid used and the common salt formed by the decomposition. The process of dialysis furnishes the means of separating these latter substances without causing the precipitation of the silicic acid, which is left in the dialyser in the form of a colourless limpid solution. This solution is, however, very unstable, especially when concentrated, and the addition of even very minute quantities of various salts causes the whole of the silica to separate out in the form of a translucent jelly, which cannot be re-dissolved, except by the addition of a fresh quantity of alkali.

Liquid stannic, titanic, tungstic, and molybdic acids have been prepared by a similar process.

If in such experiments as those just described, the solution of a salt or of sugar is placed, not in an open dialyser but in a bladder, inclosed in a porous vessel which prevents the bladder from stretching, and a glass tube attached to the neck of the bladder, it will be seen on immersing the

whole in water that the liquid rises in the tube above the level of the liquid outside. This rise indicates the existence of a pressure in the solution which has been called *osmotic pressure.* A slight modification of this experiment will permit of the exact measurement of the amount of this pressure in solutions of different substances and of different strengths. The water is capable of passing freely through the membrane, but the dissolved substance diffuses outwards only very slowly. Hence water passes inwards till the pressure of the water on both sides of the membrane is the same, and inside there is the additional pressure, the osmotic pressure, of the dissolved substance.

9. All the foregoing facts are explained by the hypothesis that substances in solution consist of very small moving particles, which behave as though they were in the gaseous state. It is in fact found that the laws which regulate osmotic pressure have the same form as the laws of Boyle, of Gay-Lussac, and of Avogadro which relate to gases.

Thus temperature being kept constant, osmotic pressure is proportional to the strength of the solution, and by the strength of the solution is meant the amount of substance in unit volume of the liquid. This corresponds to gas pressure, which is proportional to the mass of gas in unit volume of space.

A solution of sugar has been shown to give the following pressures, which, allowing for experimental error, are obviously proportional to the matter dissolved :—

Strength of solution.	Pressure.
1 per cent.	53·5 c.m. of mercury
2 „	101·6 „
2·74 „	151·8 „
4 „	208·2 „
6 „	307·5 „

In like manner osmotic pressure is related to tempera-

ture, being proportional to the absolute temperature if the volume is kept constant. This is the law of Gay-Lussac and Charles applied to solutions, and changes of pressure for given changes of temperature may be calculated by using the same coefficient, namely $\frac{1}{273}$ or 00366, as in the case of gases. One example will suffice. A solution containing 1 per cent. of cane sugar was found to give at 36° C. a pressure equal to 56·7 centimetres of mercury, and the same solution at 15·5° gave a pressure of 52·1 c.m. The pressure calculated for this difference of temperature is 52·9 c.m., which is near enough to the experimental result to show that the formula holds good for weak solutions.

A solid or liquid dissolved in a liquid then behaves as though it existed as a gas in a space equal to that occupied by the solution. When different solutions are compared, it is found that the osmotic pressure is generally the same when the solutions contain in equal volumes quantities of dissolved substances proportional to their molecular weights. This is equivalent to the statement that the law of Avogadro holds good for solutions. Some important exceptions to this generalisation are noticeable among salts, but these exceptions are accounted for by the hypothesis of ionic dissociation, which accounts for the greater effect produced by the assumption that the number of active molecules in unit volume is doubled in completely dissociated substances. The analogy between a gas and the state of a dissolved substance is now universally recognised. Osmotic pressure is the cause of liquid diffusion and the dialytic separation of dissolved substances, but, as already explained, these processes are very slow.

The act of dissolution and the state of saturation may be explained as follows: A solid immersed in a liquid receives upon its surface the moving molecules of the liquid, and as a result some of the molecules from its surface may become detached and carried off into the liquid. If the encounters of the liquid molecules with those

of the solid are incompetent to remove any of them, the substance is insoluble. Once in the liquid the molecules of the dissolved substance may be supposed to move about after the manner of liquid molecules, either singly or in groups, or in company with some of the molecules of the solvent. According to this, the process of dissolution is analogous to the process of evaporation, and just as in the case of evaporation we conceive that molecules which are near to the liquid surface may get entangled there and return to the liquid state again, so we must believe that, so long as a portion of the solid remains undissolved in the liquid, there is an interchange taking place between the liquid and solid molecules near its surface. If temperature is raised the process of dissolution is usually promoted, for the molecules of both liquid and solid are more strongly agitated, and the cohesion between the particles of the solid is diminished. But for every given temperature there is a limit to the amount of solid dissolved (in all ordinary cases), when the number of molecules of solid passing off into the liquid no longer exceeds the number of molecules which return from the liquid to the solid surface and are retained there.

Naturally connected with the production of solutions is the process of crystallisation, as it is in the gradual passage from the liquid to the solid state that we find the most generally useful method for the formation of crystals.

The crystallisation of a crystallisable solid from its solutions occurs when the percentage of solid present in the liquid exceeds a certain limit dependent on the nature both of the solid and the liquid in which it is dissolved. This condition may be brought about either by allowing part of the solvent to evaporate, or by altering, in general by lowering, the temperature. Crystals are then formed, and these crystals frequently contain not only the elements of the dissolved substance, but a portion of the solvent united to it in definite molecular proportions. This is particularly

noticeable in the case of aqueous solutions, and the water thus combined is spoken of as *water of crystallisation.* Alcohol and benzene, and probably other liquids, unite with salts and other crystallisable bodies in the same manner. It is noteworthy that the proportion of water of crystallisation is principally dependent upon the temperature at which the process of crystallisation takes place. Thus, sulphate of sodium crystallises from water at temperatures above 34° in the anhydrous state. But at the ordinary temperature of the air, the solution deposits crystals which contain ten molecules of water with one molecule of the salt.

Certain solutions refuse to crystallise when cooled down below the temperature at which, under ordinary circumstances, they yield crystals. Such liquids are said to be *supersaturated.* In order to prepare a supersaturated solution it is only necessary to warm some water gently in a test-tube or flask and add to it crystals of sodium sulphate or of alum, or sodium carbonate, so long as they are dissolved. If the solution is then filtered clear, covered to protect it from dust, and allowed to cool, it will generally remain liquid. If now a small particle of the same salt be dropped into the liquid, crystallisation at once commences, and proceeds so rapidly that in a few minutes the whole sets into a solid mass. In most cases crystallisation is not started by shaking the liquid, nor by the introduction of a crystal of a different salt, unless it be strictly isomorphous with the dissolved substance.

Absorption of Gases.—All gases dissolve to a greater or less extent in water, but, unlike solids, their solubility diminishes as the temperature rises, so that in most cases [1] the dissolved gas may be completely expelled from a liquid by boiling, while the amount taken up may be greatly increased by cooling the liquid.

[1] Exceptions occur in the cases of hydrogen chloride and some other gases.

Increase of pressure also augments the solubility of gases in a direct ratio. It is therefore necessary in making any statement as to the solubility of a gas to observe the conditions of temperature and pressure under which that solubility was estimated. The following examples will serve to show how greatly gases differ in the extent to which they dissolve in water.

At 0° C. and under a pressure of 760 mm. barom.
1 volume of water will dissolve

Hydrogen	·0193
Nitrogen	·02035
Oxygen	·04114
Nitrous oxide	1·3052
Carbon dioxide	1·7967
Hydrogen sulphide	4·3706
Sulphur dioxide	79·789
Ammonia	1148·8

The numbers given above represent volumes of the several gases measured at 0° and 760 mm., and constitute the *coefficients of absorption* of these gases at that particular temperature and pressure.

The general statement that the weight of a gas dissolved by a liquid is directly proportionate to the pressure is often known as the law of Henry and Dalton. It admits of another expression; for since, according to the law of Boyle, the volume of a gas diminishes as the pressure upon it increases, it is obvious that the volume of gas thus held in solution must always be the same, whatever the pressure.

These rules no longer hold good when the gas and the liquid exert a chemical action upon each other, and exceptions must also be recognised in the case of the more soluble gases, such as hydrogen chloride and ammonia.

The determination of the absorption of gases by liquids may be applied in certain cases to the elucidation of some important theoretical and practical questions. Atmospheric

air furnishes an example which will be worth the consideration of the student.

When a mixture of gases is exposed to the action of a solvent, the quantity of each of the constituents dissolved by the liquid will depend first upon its coefficient of solubility, and secondly upon the proportion in which it exists in the mixture. This proportion determines the pressure which each gas present exerts upon the surface of the liquid, and consequently regulates the amount of it which is dissolved. The total pressure produced by the mixture is therefore the sum of those partial pressures due separately to the individual constituents. To make this more clear:

Suppose a very large vessel, containing a very little water, and filled with oxygen, under a pressure of one atmosphere. It is plain that if four-fifths of the gas were removed the pressure would be reduced to one-fifth of an atmosphere, and the quantity of oxygen dissolved would be only one-fifth the quantity taken up under the previous conditions, provided, of course, that the temperature remain constant. An exactly similar vessel can be conceived filled with nitrogen under one atmosphere, and containing a little water. If one-fifth of the nitrogen were removed, the pressure of the remainder would be only four-fifths of an atmosphere, and the quantity dissolved would be reduced to four-fifths. Lastly, a similar vessel, filled with atmospheric air, contains a gas in which the conditions of the two previously supposed experiments are combined.

Air is composed very nearly of four volumes of nitrogen to one volume of oxygen, and by reason of the greater solubility of oxygen the proportion of the two gases one to the other is found to be disturbed when air is shaken up with water, the dissolved gas being richer in oxygen, the residual air richer in nitrogen, than the original.

No stronger evidence could be adduced in favour of the view generally held, that in atmospheric air the two main

components are not united chemically, but are in a state of intimate mechanical mixture.

Note.—The following is an example of the kind of problem that might occur in connection with this subject:

Calculate the percentage composition of the gas which would be dissolved by water exposed in a room full of air containing 79 N, 20·6 O, and ·4 of CO_2 in 100 volumes (temp. 0° and bar. 760 mm.).

Coeff. of sol. for oxygen	·04
" " nitrogen . . .	·02
" " carbon dioxide . .	1·79

The pressures are proportional to the volumes of the gases present. Therefore the relative quantities dissolved would be:

Nitrogen	79	×	·02	=	1·58
Oxygen	20·6	×	·04	=	·824
Carbon dioxide	·4	×	1·79	=	·716
		The total quantity	.	=	3·120

The percentage composition of the dissolved gas would therefore be:

Nitrogen	50·6
Oxygen	26·4
Carbonic dioxide	22·9

CHAPTER XXI.

GENERAL SUMMARY.

In this concluding chapter it will be useful to the student, who is in danger of being confused by the large array of facts and the multiplicity of hypotheses necessarily involved in the study of chemistry, to review in somewhat general terms the fundamental principles which may be regarded as fully established, and the theories which are now accepted by the great majority of chemists.

In the first place we may consider that chemistry has contributed more than any other branch of science to the establishment of the two great principles which underly all physical science, namely, the *conservation of matter* and the *conservation of energy*. Various attempts have been made to prove that in certain cases of chemical combination a diminution of mass occurs, but all that has really been shown is that a very slight loss of weight is supposed to have been observed, which, in the absence of further evidence, may safely be put down to errors of experiment. The work of thousands of analysts daily testifies, at any rate, their belief, that when chemical combination or decomposition takes place no gain or loss of material is incurred, and that the sum of the masses engaged in any chemical change is constant throughout that change.

The laws of definite, multiple, and reciprocal proportions by weight (pp. 35, 44, 45) are accounted for completely by the idea of the *atomic* structure of matter introduced by Dalton in 1808, and the methods by which are estimated atomic and molecular weights, that is the *relative masses of atoms and of molecules*, which are made up of atoms, now form the basis of the most familiar of laboratory operations.

In the early days of chemical development, nearly a century ago, it was believed that the properties of bodies depended solely upon the nature of the elements of which they were composed. But the discovery of the phenomena of isomerism about 1830 led to the recognition of the fact that not only the nature but the number and *arrangement of the atoms in a compound determine its character*. In other words, the properties of compounds depend upon their chemical structure, which is displayed, though doubtless imperfectly, in the formulæ now familiar to every student. A very important generalisation in regard to the elements themselves has gradually been recognised and embodied in the statement usually known as the Periodic

Law, from which we learn that *the properties of the elements are, in general, periodic functions of their atomic weights.*

And further, chemists are not only familiar with the notion that all matter is composed of minute indivisible particles, but it is universally believed that the *arrangement of atoms in space* can be determined with some degree of assurance. The fundamental ideas and methods of stereochemistry have now been extended to the compounds of nitrogen, sulphur, and several metals, so that it is no longer necessary to suppose that the phenomena which have been specially studied during the last thirty years are limited to the compounds of one element carbon.

The belief that chemical combination takes place between atoms of matter, and that in the compounds thus formed the individual atoms retain in some degree their independence, is generally adopted by chemists. But why they combine at all, why a given atom possesses the power of selecting other atoms from a group presented to it, and why an atom habitually associates with one, two, three, or more atoms of another kind (valency), are questions which in the present state of knowledge cannot be answered.

Two principal theories have been proposed to account for the acts of chemical combination and decomposition. The earlier of these, introduced by Davy, modified by Berzelius, and supported by Faraday, represents the act of union between two atoms as the result of the attraction caused by opposite charges of electricity resident upon them. The other view, introduced by Williamson in 1850, regards chemical change as due to the continual movement of the molecules concerned, and their frequent temporary disruption into parts which, during a longer or shorter period, according to circumstances, are supposed to be entirely independent, but when an opportunity occurs enter again into union. According to this hypothesis chemical combination is probably due to a harmony or similarity of movement in the atoms which become joined

together. These ideas have already been explained in Chapter XIX. In order to examine further the ground for these hypotheses it will be useful to recall briefly the chief conditions which affect the exercise of that form of energy which gives rise to chemical combination, or what is still commonly called 'chemical affinity,'[1] and to state concisely its correlation with other forms of energy.

1. It acts only at inappreciable distances, smaller than any which can at present be measured. Atoms chemically united are probably not in actual contact with each other, but are separated by a distance which is at least several times their own diameters. If this is true, the attraction which they exert upon each other must be believed to involve some action in the medium which fills the space between them, as in the case of other attractions at a distance, such as that due to electrical or magnetic induction.

2. It is selective, that is, it is not exercised indifferently between any two or more substances brought together, but is usually manifested most actively between elements which are at the opposite extremities of the electro-chemical series. The halogens and oxygen, for example, unite most vigorously with the alkali metals and form compounds with them more stable than with any other element.

3. Chemical change, whether combination or decomposition, is attended by a concentration or dissipation of energy, indicated usually by absorption or evolution of heat.

4. Chemical affinity differs from gravitation not only in not operating at all distances, but in the fact that two or more atoms, having combined together, lose more or less completely the power of attracting other atoms. Gravitation acts not only between a given body and one other, but

[1] The word affinity seems to have arisen from a notion current among the early chemists, that when two bodies are capable of combining there must be some resemblance or affinity between them, or that they contain some principle common to them both.

between that body and all others, so far as we know, in the universe.

5. Chemical compounds are broken up by heat. A large number of facts have already been set forth in the chapter on Thermal Dissociation. Considering the action of rise of temperature on any substance, it appears probable that the first effect is to cause expansion, that is, the molecules separate to a greater distance from one another, then the atoms become rearranged into new combinations, more stable, and usually more simple in structure, till ultimately, when the temperature is high enough, the atoms are themselves separated and chemical combination is at an end.

6. It was formerly supposed that the elements were separable from chemical compounds by an electric current. The hypothesis now generally adopted assumes that the act of separation of ions, which may be elemental or not, is accomplished when the substance is rendered liquid or gaseous, by solution, by fusion, or by vaporisation according to circumstances. By the same hypothesis the liberation of the ions is due to opposite electrical charges which are developed on the ions when they separate, so that the current does no more than drive them to the electrodes, where they are discharged and become electrically neutral.

7. Chemical combination is not in all cases distinguishable from what is called adhesion. Adhesion, like chemical affinity, is elective, as shown by such facts as that glass is wetted by water though not by mercury, which sticks only to metals with which it can combine. Again, if a drop of a solution containing a mixture of cadmium and mercuric chlorides is placed upon filter paper, and allowed to spread, the cadmium extends further into the paper than the mercury, as may be shown by exposing the stain to sulphuretted hydrogen, when a yellow ring of cadmium sulphide is formed outside the dark mercuric sulphide.

Again, chemical compounds may be decomposed not only by the operations usually considered to be exclusively

chemical, but also by agents commonly regarded as non-chemical or mechanical. Thus lead acetate and lead nitrate, tartar emetic, and ammonio-sulphate of copper, may be completely deprived of their respective metals if a solution of each salt is shaken up with pure carbon from bone charcoal.

It might be supposed that the relatively greater stability of chemical union would be a sufficient guide if such facts as the copious absorption of hydrogen by palladium and the condensation of bromine vapour, ammonia, and other gases by porous bodies, especially hard charcoal, did not show that so-called adhesion may be equally persistent.

Relative stability evidently fails as a distinctive characteristic of chemical combination when we consider the properties of such a series of compounds as the following:—

SCl_4, PH_4Br, NH_4HS, NH_4Cl, Hg_2Cl_2, $CaCO_3$, SiO_2.

At the one end of this series are compounds of which the components cannot remain united even at ordinary atmospheric temperature and pressure, while at the other end are compounds which bear a high temperature and contact with many other substances without change.

The more stable forms of chemical combination such as give rise to the host of oxides, chlorides, salts, and carbon compounds are distinguished by constancy of composition and the possession of definite physical characters, but the law of definite proportions cannot always be used as a means of distinguishing chemical combination.

Beginning with ordinary cohesion, in virtue of which similar particles are attached to one another, and adhesion—which is the name given to the unknown cause of the union of dissimilar particles—and passing in review the various phenomena of absorption, occlusion of gases by solids, and solution, we arrive by imperceptible de-

grees at the compounds which have been long distinguished by many chemists as 'molecular' compounds, in which entire molecules have been supposed to be united together by a special kind of chemical affinity. This distinction is, however, now rapidly disappearing, as it is acknowledged that there is no character by which compounds of water or of ammonia with salts, of iodine with iodides, or of salts with one another, can be sharply distinguished from those in which atoms are supposed to be linked together by ordinary chemical affinity.

The more stable forms of combination seem to result from a comparatively close approximation of the constituent atoms or molecules, which is indicated by differences of density. Thus the specific volume of 'water of halhydration' (as it was called by Graham) in the sulphates of the magnesium group is less than the 'water of crystallisation,' each additional molecule of which occupies a gradually increasing volume.

The following table shows the mean specific volumes of MSO_4nH_2O, where M is Cu, Mg, Zn, Ni, Co, Mn, or Fe :—

Value of *n*.	Mean Specific Volume of MSO_4nH_2O.	Molecular Volume of *n*th mol. of H_2O.
0	44·8	—
1	55·5	10·7
2	68·8	13·3
3	83·3	14·5
4	98·7	15·4
5	112·9	14·2
6	130·0	17·1
7	146·1	16·1

These last figures approach the specific volume of ice, which is $\frac{\text{Mol. Wt.}}{\text{Dens.}} = \frac{18}{92} = 19·6$, that of liquid water being 18.

When these salts are dissolved in water the water of

crystallisation acquires the same volume per molecule as the rest of the water in the solution.

Again, when lead replaces silver, or potassium replaces sodium in the nitrate, or when chlorine replaces bromine or iodine in combination with another element, contraction occurs. And in general contraction is observed when an element of reputed strong affinity (as indicated by the amount of heat evolved when it enters into combination) takes the place of one of reputed smaller affinity. The following examples will suffice :—

Molecular Weight.	Density.	$\frac{\text{Mol. Wt.}}{\text{Dens.}}$ = Mol. Vol.
AgCl = 143·5	5·517	26·0
$\frac{1}{2}PbCl_2$ = 139	5·78	24·0
NaI = 150	3·45	43·5
NaBr = 103	2·952	34·8
NaCl = 58·5	2·148	27·2

There can be no doubt that the formation and continued existence of many compounds is a question of space and hence is connected with the atomic weight of one or other of the elements concerned. Thus the alkali metals are known to be capable of forming many compounds with the halogens, in which more than one atom of the halogen is combined with each atom of metal. But the stability of such compounds seems to depend upon the atomic weight of the metal, for while, for example, potassium is capable of forming a somewhat unstable tri-iodide KI_3, and no bromide, except the monobromide KBr, cæsium is capable of forming a stable crystallisable pentiodide, CsI_5, and pentabromide $CsBr_5$. On the other hand, cases are known among carbon compounds in which, while chlorine is introduced very easily, the product containing an equivalent quantity of bromine is obtainable with great difficulty or not at all.

The fact that in a series of salts containing metals of the

same family, such as calcium, strontium, and barium, or magnesium, zinc, and cadmium, the amount of water of crystallisation depends on the metal is probably a phenomenon of the same order, and seems to depend upon the packing together of the constituents of the molecule. Carbon compounds, however, afford the best examples of the relation of constitution to space, but reference to these must be deferred till the student is familiar with 'organic' chemistry.

As to the relative strength or force of affinity between two atoms in different cases, there is much apparent conflict of evidence. Common experience seems to indicate that the strength of the affinity between different atoms varies according to their nature. Thus an iodide is decomposed by bromine or by chlorine with liberation of iodine. Here, however, the student must be again reminded that the change is not correctly represented as



$$HI + Br = HBr + I.$$

And though at first sight it seems to depend upon the tendency for H to combine with Br in preference to I, to this must certainly be added the affinity of I for I, the interaction probably proceeding in two stages, thus :





$$\begin{aligned} HI + BrBr &= HBr + IBr \\ HI + IBr &= HBr + II. \end{aligned}$$

Little can be inferred even from the replacement of one metal by another, as of mercury by copper, copper by iron, &c., in solutions of their salts, for in all these cases the process is complicated by electrical effetcs, or by a difference of physical condition between the materials and the products of their interaction, also by the relative masses of the acting ingredients.

It has been supposed that the amount of heat evolved during the formation of series of compounds in which only

one element varies might serve as a measure of the relative affinities of the several interchangeable elements, as, for example, in the interchange of metals or of halogens for one another (p. 303). But though unquestionably differences are manifest in such cases, it does not follow that the different amounts of energy degraded in the process of combination indicate that the atoms combining come together with different amounts of force, for the loss may be due to changes in the configuration or motion of the atoms themselves.

On the whole, the hypothesis that chemical combination, as well as adhesion and cohesion, is due to a state of motion of the atoms or molecules engaged in a given operation deserves perhaps most consideration. This view conforms with all that is known concerning the mechanical properties of gases; it explains the phenomena of dissociation, and without it the influence of 'mass' upon chemical processes would be unintelligible. The relatively great stability of the molecules of the so-called 'elements' (*e.g.* N_2, O_2, &c.) in which the component atoms are alike seems also explicable on the hypothesis that this stability is due to a similarity or harmony of their motions rather than to anything in the nature of an electrical charge.

EXERCISES ON SECTION III.

1. Water is shaken up with a large volume of oxygen gas under a constant pressure of 765 mm. What volume of the gas will be contained in 10 c.c. of the solution?

2. Water is exposed to an atmosphere consisting of 21 vols. of oxygen, with 79 volumes of nitrogen.

Temp. 0°; pressure, 760 mm.
Coeffs. of sol., N = ·02, O = ·04.

Calculate (*a*) the total volume of gas dissolved by 52·5 c.c. of water, and (*b*) the percentage composition of the gas.

3. Soda-water is charged under a pressure of 2·3 atmospheres. Calculate the volume of carbon dioxide contained in 300 cubic centimetres of such water.

An atmosphere = 760 mm. barom.
Coeff. of sol. for carbon dioxide, 1·7967.

4. Sulphur dioxide is passed into water as long as it is absorbed. If the barometer stands at 745 mm., calculate the volume of gas contained in half a litre of the solution.

Coeff. for sulphur dioxide, 79·789.

5. Water is shaken up with its own bulk of a mixture of 1 volume of oxygen with 3 vols. of nitrogen. Supposing the temp. and pressure to remain normal and constant throughout the experiment, calculate the composition of the residual air.

Coeff. of oxygen. ·04114.
Coeff. of nitrogen, ·02035.

6. The density of the vapour of ammonium chloride is said to be abnormal. Explain this statement, and describe the experimental evidence upon which it is based.

7. Give some examples of the influence of 'mass' in determining chemical reactions, and explain them.

8. Ammonium carbonate and calcium chloride are dissolved in separate portions of water, and the solutions are then mixed. Express the result by an equation.

Ammonium chloride and chalk, both dry, are mixed together and heated. Express the result by an equation.

How do you explain such apparently inconsistent phenomena?

9. In an experiment in which iron was heated in steam show that the following observations of pressure are in accordance with theory:—

Temp.	Steam	Hydrogen.
t°	46 mm.	2·8 mm.
T°	101 mm.	579 mm.

10. Referring to the table of heat of formation of chlorides (p. 303), determine which of the metals, zinc, cadmium, mercury, copper, gold, will decompose aqueous hydrochloric acid, and range them in their apparent order of affinity for chlorine.

11. What substances and what relative quantities of each will be formed by passing the same current through solutions in water of potassium iodide, copper sulphate, hydrochloric acid (strong), and hydrochloric acid (dilute)?

12. A current of electricity is passed simultaneously through solutions of cupric and cuprous chloride. How much copper and how much chlorine are liberated from the cuprous chloride for every molecule of cupric chloride decomposed by the current? In what relation do these quantities stand to the quantity of zinc consumed in each cell of the battery, secondary actions being neglected?

13. What weight of water would be heated from 0° to 1° by the combustion of 1 gram of charcoal in oxygen?

14. What weight of water would be heated from 0° to 15° by the combustion of 1 gram of hydrogen in chlorine?

15. Calculate the temperature of combustion of phosphorus burning

16.

Heat of combustion of hydrogen	34034	units.
Latent heat of steam at 100° .	537	,,
Specific heat of steam . .	·475	unit
Specific heat of nitrogen . .	·2438	,,

Composition of air, N 77, O 23 parts by weight.

With these data find the temperature of the hydrogen flame burning in air.

17. What weight of water at 100° would be turned into steam by the combustion of 1,000 kilograms of coal containing—

Carbon	90·7	per cent.
Hydrogen	4·3	,,
Oxygen and nitrogen	4·0	,,
Incombustible ash	1·0	,, ?

Assume the heat of combustion of C and H as given in the table on p. 310. Latent heat of steam at 100° = 537.

18. The heat of combustion of 1 part by weight of marsh-gas is 13,000. What weight of ice will be melted by the heat produced by the combustion of a litre of the gas measured at normal temperature and pressure?

Latent heat of water at 0° = 79

19. What volume (calculated at 0° and 760 mm.) of producer gas consisting of—

Carbonic oxide	25 per cent.
Hydrogen	5 ,,
Marsh-gas	4 ,,
Carbon dioxide	6 ,,
Nitrogen	60 ,,

must be burned in order to convert 2,000 kilograms of water at 0° into steam at 100°?

Heat of combustion of marsh-gas = 13,000.

20. From the following data obtained by Victor Meyer's process, calculate the vapour density and molecular weight of phosphoric oxide—

Weight of substance	·1904 gram.
Volume of expelled air at 15° and 749 mm. .	15·73 c.c.

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I. NAMES OF CHEMISTS AND PHYSICISTS.

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CHEMICAL PHILOSOPHY

ANSWERS TO THE PROBLEMS

ANSWERS TO PROBLEMS.

Solutions are not supplied in those cases in which the answer is to be found plainly stated in the text, nor to those few questions which require for a satisfactory answer a lengthy discussion.

ANSWERS TO PROBLEMS

IN

TILDEN'S

CHEMICAL PHILOSOPHY.

SECTION

1. 94·93 c.c.
2. 256·71 c.c.
3. 14·42 atmospheres.
4. 1033·296 grams, or 1 kilo and 33·296 grams.
5. 101970 grams, or 101 kilos and 970 grams.
6. 16·3152 grams per sq. centimetre.
7. ·1650 gram.
8. 1·2544 gram ; 19·712 grams ; ·3584 gram.
9. 107·3 c.c. ; 105·6 c.c. ; 136·6 c.c.
10. If V be the volume at 75°, it will be ·7844 V at 0°.
11. 1218·9 c.c.
12. 553 c.c.
13. 264·7 c.c.
14. 53·26 c.c.
15. −77°·6.
16. $\frac{5}{2457}$, or ·002036.
17. 142·03 c.c.
18. 58·38 c.c.
19. 590·9 mm.

20. 130·49 litres.

21. Chlorine to hydrogen ·1678 to 1, or nearly 1 to 6.

22. Hydrogen, 1 : carb. dioxide, ·2132 : ozone, ·2041.

23. 1·52 (air = 1), or 21·9 (hydn. = 1).

24. ·9575.

25. An approximate solution is obtained as follows :—

At the end of the 1st second the hydrogen which has entered is 3·83, whilst the oxygen which has escaped is $\frac{1}{4}$ of 3·83, or ·96. The composition of the mixture is therefore

$$19{\cdot}04\ \mathrm{O} + 3{\cdot}83\ \mathrm{H}.$$

Assuming that the supply of hydrogen outside is indefinitely large, inter-diffusion will then occur between hydrogen and a mixture consisting of

$$\frac{3{\cdot}83}{22{\cdot}87}\ \mathrm{H}\ \text{and}\ \frac{19{\cdot}04}{22{\cdot}87}\ \mathrm{O}.$$

The hydrogen which returns outwards from this mixture in the next second is

$$\frac{3{\cdot}83}{22{\cdot}87}\ \text{of}\ 3{\cdot}83,\ \text{or}\ {\cdot}64\ \text{c.c.},$$

and the oxygen escaping is

$$\frac{19{\cdot}04}{22{\cdot}87}\ \text{of}\ {\cdot}96,\ \text{or}\ {\cdot}8\ \text{c.c.}$$

At the end of the 2nd second, therefore, the mixture will consist of—

	Oxygen		Hydrogen
	$(19{\cdot}04 - {\cdot}8)$	+	$(3{\cdot}83 - {\cdot}64 + 3{\cdot}83)$
or	$18{\cdot}24$	+	$7{\cdot}02.$

Proceeding in the same manner, the hydrogen entering in the 3rd second is 3·83.

The hydrogen escaping is

$$\frac{7{\cdot}02}{25{\cdot}26}\ \text{of}\ 3{\cdot}83 = 1{\cdot}06.$$

The oxygen escaping is

$$\frac{18·24}{25·26} \text{ of } ·96 = ·69.$$

Whence at the end of the 3rd second the mixture is

$$\overset{\text{Oxygen}}{(18·24-·69)} + \overset{\text{Hydrogen}}{(7·02-1·06+3·83)}$$

or $17·55 + 9·79$

26. Calculate first the amount of A which in each compound is combined with one part of B :—

thus

$$\frac{96·28}{3·72} = 25·88 \quad . \quad . \quad . \quad . \quad \text{I.}$$

$$\frac{92·83}{7·17} = 12·94 \quad . \quad . \quad . \quad . \quad \text{II.}$$

$$\frac{89·62}{10·38} = 8·63 \quad . \quad . \quad . \quad . \quad \text{III.}$$

$$\frac{86·62}{13·38} = 6·47 \quad . \quad . \quad . \quad . \quad \text{IV.}$$

These quotients evidently stand towards one another in the ratios

	I.		II.		III.		IV.
	4	:	2	:	1·33	:	1
or	12	:	6	:	4	:	3

which are in the simple relation required by the law. Or A may be made unity in each case, and the proportion of B calculated in a similar manner.

27. Proceed as in the last exercise. Then

100 N are combined with 50 O
100 " " " 100 "
100 " " " 200 "

From which it is obvious that

50 : 100 : 200 as 1 : 2 : 4.

30. O represents one atom of oxygen.

O_2 represents one molecule of oxygen, consisting of two atoms.

		Molecules		Each consisting of
OH_2	represents	1	of water	1 atom of oxygen. 2 atoms of hydrogen
$2OH_2$	,,	2	,, ,,	ditto ditto
HCl	,,	1	,, hydrogen chloride or hydrochloric acid	1 atom of hydrogen 1 atom of chlorine
H_2	,,	1	,, hydrogen	2 atoms of hydrogen
Cl_2	,,	1	,, chlorine	2 atoms of chlorine
NH_3	,,	1	,, ammonia	1 atom of nitrogen 3 atoms of hydrogen
H_3PO_4	,,	1	,, hydrogen phosphate or phosphoric acid	3 atoms of hydrogen 1 atom of phosphorus 4 atoms of oxygen
H_2SO_4	,,	1	,, hydrogen sulphate or sulphuric acid	2 atoms of hydrogen 1 atom of sulphur 4 atoms of oxygen
$FeSO_4$	,,	1	,, ferrous sulphate	1 atom of iron 1 atom of sulphur 4 atoms of oxygen
$2FeSO_4$	,,	2	,, ,, ,,	ditto ditto
$Al_2(SO_4)_3$	,,	1	,, aluminium sulphate	2 atoms of aluminium 3 atoms of sulphur 12 atoms of oxygen
$12OH_2$	,,	12	,, water	1 atom of oxygen 2 atoms of hydrogen
$12Al_2(SO_4)_3$	,,	12	,, aluminium sulphate	as above
CO_2	,,	1	,, carbon dioxide or carbonic anhydride	1 atom of carbon 2 atoms of oxygen
$3CO_2$	,,	3	,, ditto ditto	ditto ditto

		Formula	Molecular Weight
31.	Water	OH_2 or H_2O	18
	Ammonia	NH_3	17
	Hydrochloric acid	HCl	36·5
	Carbonic anhydride	CO_2	44
	Sulphuric acid	H_2SO_4	98
	Ferrous sulphate	$FeSO_4$	152
	Aluminic sulphate	$Al_2(SO_4)_3$	342·6
	Phosphoric acid	H_3PO_4	98

32	$2HgO$	= 432
	$10OH_2$	= 180
	$3FeS$	= 264
	$3FeS_2$	= 360
	$2CS_2$	= 152
	$KC_4H_5O_6$	= 188
	$K_2C_4H_4O_6$	= 226
	$5C_7H_9N$	= 535
	$12CH_4$	= 192
	$KAl(SO_4)_2 + 12OH_2$	= 474
	$3[NH_4Cr(SO_4)_2 + 12OH_2]$	= 1434
33.	BaO	Barium monoxide (baryta).
	CaO	Calcium monoxide (lime).
	MgO.	Magnesium monoxide (magnesia).
	ZnS	Zinc sulphide.
	KCl	Potassium chloride.
	$NaBr$	Sodium bromide.
	AgF	Silver fluoride.
	H_2S	Hydrogen sulphide (sulphuretted hydrogen).
	HI	Hydrogen iodide (hydriodic acid).
	KCN or KCy	Potassium cyanide.
	SSe	Sulphur selenide.
	BN	Boron nitride.
	H_3P	Hydrogen phosphide (phosphine).
34.	BaO	Barium monoxide.
	BaO_2	Barium dioxide.
	Hg_2O	Mercurous oxide.
	HgO	Mercuric oxide.
	FeS	Iron monosulphide or ferrous sulphide.
	FeS_2	Iron disulphide (iron pyrites)
	MnO	Manganese monoxide, or manganous oxide.
	Mn_2O_3	Manganese sesquioxide, or manganic oxide.
	MnO_2	Manganese dioxide, or manganic peroxide.
	FeO	Iron monoxide, or iron protoxide, or ferrous oxide.

Fe_2O_3	Iron sesquioxide, or iron peroxide, or ferric oxide.
$Fe_3O_4 = FeO + Fe_2O_3$	Ferroso-ferric oxide (magnetic oxide of iron).
N_2O	Nitrogen monoxide, or nitrous oxide.
N_2O_2	Nitrogen dioxide, or nitric oxide. (For the formula of nitric oxide, see p. 107.)
N_2O_3	Nitrogen trioxide, or nitrous anhydride.
N_2O_4	Nitrogen tetroxide, or nitric peroxide.
N_2O_5	Nitrogen pentoxide, or nitric anhydride.
P_2S_3	Phosphorus trisulphide, or phosphorous sulphide.
P_2S_5	Phosphorus pentasulphide, or phosphoric sulphide.
$SnCl_2$	Tin dichloride, or stannous chloride.
$SnCl_4$	Tin tetrachloride, or stannic chloride.
$FeBr_2$	Ferrous bromide.
Fe_2Br_6	Ferric bromide.
Cu_2Cl_2	Cuprous chloride.
$CuCl_2$	Cupric chloride.
$CrCl_2$	Chromous chloride.
Cr_2Cl_6	Chromic chloride.
CrF_6	Chromium or chromic hexfluoride.
$SbBr_3$	Antimony tribromide or antimonious bromide.
$SbBr_5$	Antimony pentabromide or antimonic bromide.
35. KNO_2	Potassium nitrite.
KNO_3	Potassium nitrate.
K_2SO_3	Potassium sulphite.
K_2SO_4	Potassium sulphate.
KCl	Potassium chloride.
$KClO$	Potassium hypochlorite.
$KClO_2$	Potassium chlorite.
$KClO_3$	Potassium chlorate.
$KClO_4$	Potassium perchlorate.

KI	Potassium iodide.
KIO_3	Potassium iodate.
KIO_4	Potassium periodate.
$NaHSO_3$	Sodium hydrogen sulphite.
Na_2SO_3	Sodium sulphite.
Na_2HPO_4	Disodium hydrogen phosphate.
Na_3PO_4	Trisodium phosphate.
NaH_2PO_4	Sodium dihydrogen phosphate.
H_3PO_2	Hypophosphorous acid, or hydrogen hypophosphite.
H_3PO_3	Phosphorous acid or hydrogen phosphite.
H_3PO_4	Phosphoric acid or hydrogen phosphate.
HCl	Hydrochloric acid or hydrogen chloride.
$HClO$	Hypochlorous acid or hydrogen hypochlorite.
$HBrO$	Hypobromous acid or hydrogen hypobromite.
$HClO_2$	Chlorous acid or hydrogen chlorite.
$HClO_3$	Chloric acid or hydrogen chlorate.
HIO_3	Iodic acid or hydrogen iodate.
$HClO_4$	Perchloric acid or hydrogen perchlorate.
$HBrO_4$	Perbromic acid or hydrogen perbromate.

36.

	No. of mols.	Name	Weight of 1 mol.	Whole weight used	Whole weight obtained
a. MnO_2	1	Manganese dioxide	87	87 } = 233	
$4HCl$	4	Hydrochloric acid	36·5	146	
$MnCl_2$	1	Manganese chloride	126		126 } = 233
Cl_2	1	Chlorine	71		71
$2H_2O$	2	Water	18		36
b. $2KI$	2	Potassium iodide	166·1	332·2 } = 403·2	
Cl_2	1	Chlorine	71	71	
$2KCl$	2	Potassium chloride	74·6		149·2 } = 403·2
I_2	1	Iodine	254		254
c. SO_2	1	Sulphur dioxide	64	64 } = 171	
$2OH_2$	2	Water	18	36	
Cl_2	1	Chlorine	71	71	
H_2SO_4	1	Sulphuric acid	98		98 } = 171
$2HCl$	2	Hydrochloric acid	36·5		73

	No. of mols.	Name	Weight of 1 mol.	Whole weight used	Whole weight obtained
d. $NaNO_3$	1	Sodium nitrate	85	85 } = 183	
H_2SO_4	1	Hydrogen sulphate	98	98	
$NaHSO_4$	1	Sodium hydrogen sulphate	120		120 } = 183
HNO_3	1	Hydrogen nitrate	63		63
e. $2MnO_2$	2	Manganese dioxide	87	174 } = 370	
$2H_2SO_4$	2	Hydrogen sulphate	98	196	
$2MnSO_4$	2	Manganese sulphate	151		302 } = 370
$2H_2O$	2	Water	18		36
O_2	1	Oxygen	32		32
f. $2K_2Cr_2O_7$	2	Potassium dichromate	294·2	588·4 } = 1372·4	
$8H_2SO_4$	8	Hydrogen sulphate	98	784	
$2K_2SO_4$	2	Potassium ,,	174·2		348·4 } = 1372·4
$2Cr_2(SO_4)_3$	2	Chromium ,,	392		784
$8H_2O$	8	Water	18		144
$3O_2$	3	Oxygen	32		96

37.

	No. of molecules	Name	Weight of 1 mol.	Whole weight	Whole volume
a. $2OH_2$	2	Water gas (steam)	18	36 used	4 used
$2Cl_2$	2	Chlorine	71	142 ,,	4 ,,
$4HCl$	4	Hydrochloric acid	36·5	146 obtd.	8 obtd.
O_2	1	Oxygen	32	32 ,,	2 ,,
b. CO_2	1	Carbon dioxide	44	44 used	2 used
C	1 *atom* Molecular weight unknown	Carbon	12 (*atomic* weight)	12 ,,	solid volume relation unknown
2CO	2	Carbon monoxide	28	56 obtd.	4
c. 2CO	2	Carbon monoxide	28	56 used	4 used
O_2	1	Oxygen	32	32 ,,	2 ,,
$2CO_2$	2	Carbon dioxide	44	88 obtd.	4 obtd.
d. $2NH_3$	2	Ammonia	17	34 used	4 used
N_2	1	Nitrogen	28	28 obtd.	2 obtd.
$3H_2$	3	Hydrogen	2	6 ,,	6 ,,
e. $2NH_3$	2	Ammonia	17	34 used	4 used
$3Cl_2$	3	Chlorine	71	213 ,,	6 ,,
N_2	1	Nitrogen	28	28 obtd.	2 obtd.
6HCl	6	Hydrochloric acid	36·5	219 ,,	12 ,,
f. NH_4NO_3	1	Ammonium nitrate	80	80 used	solid
N_2O	1	Nitrous oxide	44	44 obtd.	2 obtd.
$2H_2O$	2	Water	18	36 ,,	4 ,,

38. (*a*) $2NH_4Cl + Ca(HO)_2 = 2NH_3 + CaCl_2 + 2H_2O$.
(*b*) $NH_4NO_2 = N_2 + 2H_2O$.
(*c*) $NaCl + H_2SO_4 = NaHSO_4 + HCl$.
(*d*) $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$.
(*e*) $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$.
(*f*) $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$.

39. 64 grams and 32 grams.

40. 141·3 pounds.

41. 32·65 kilograms.

42. 137·2 pounds.

43. 265·7 pounds.

44. 28·672 grams; 159·04 grams; 190·4 grams.

45. (α) To form carbon monoxide, 1 litre; or carbon dioxide, 2 litres.

(β) To form sulphur dioxide, 1·395 litre; or sulphur trioxide, 2·0925 litres.

(γ) 9·3 or 18·6 litres.

46. 6 litres.

47. 20 litres.

48. 9·13 litres.

49. 128·7 grams.

50. 282·2 grams of crystallised oxalic acid, $H_2C_2O_4 + 2H_2O$, with about twice its weight of strong sulphuric acid.

$$H_2C_2O_4 \,.\, 2H_2O - 3H_2O = CO + CO_2.$$

51. ·9408 gram.

52. 79·87 : 20·13 :: 1 : ·2520 (black oxide),

and 88·8 : 11·2 :: 1 : ·1261 (red oxide);

also ·2520 : ·1261 :: 2 : 1.

That is the oxygen combined with unit weight of copper in the black oxide is twice as great as the oxygen combined with unit weight of copper in the red oxide; therefore, if the formula of the black oxide is CuO, that of the red oxide must be $CuO_{\frac{1}{2}}$ or Cu_2O.

Assuming the atomic weight of copper known to be 63·5, then

$$79·87 : 20·13 :: 63·5 : 16$$

and

$$88·8 : 11·2 :: 63·5 : 8$$

or

$$63·5 \times 2 : 16,$$

whence the formula is Cu_2O.

53. Calculated as in 25, the formula is OH or O_2H_2.

54. (CF)n.

55. The percentage composition is as follows:—

Nitrous oxide contains		63·63 N : 36·36 O.
Nitric oxide	„	46·66 N : 53·33 O.
Nitrous anhydride contains		36·84 N : 63·15 O.
Nitric peroxide	„	30·43 N : 69·56 O.
Nitric anhydride	„	25·92 N : 74·07 O.

The ratio $\frac{O}{N}$ is represented in these several compounds by the values ·5714, 1·143, 1·7143, 2·2859, 2·8571 or ·5714 × 1, ·5714 × 2, ·5714 × 3, ·5714 × 4, and ·5715 × 5.—Q. E. D.

The percentages may be found in some of the larger text-books of chemistry, *e.g.* Miller and Fresenius. The formula must not be used, as that assumes what is to be proved.

Similarly :

Manganous oxide contains		Mn 77·46 : O 22·54.
Red oxide	„	Mn 72·05 : O 27·95.
Manganic oxide	„	Mn 69·62 : O 30·38.
Black oxide	„	Mn 63·21 : O 36·79.

From these the weight of oxygen with unit weight of manganese in the several compounds is

·29099, ·38792, ·43637, ·58203,

which are in the ratio

1 : 1·33 : 1·5 : 2,

whence the relation is obvious.

Again :

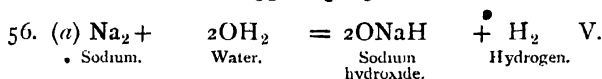
Chromous oxide	contains	Cr 76·47 : O 23·53
Intermediate oxide	,,	Cr 70·90 : O 29·10
Green oxide	,,	Cr 68·42 : O 31·58
Chromic anhydride	,,	Cr 52·00 : O 48·00

Hence the proportions of oxygen combined with unit weight of chromium are,

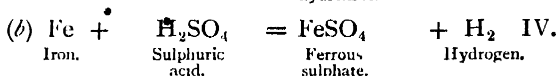
·3077, ·4104, ·4616, ·0230.

which are in the ratio of

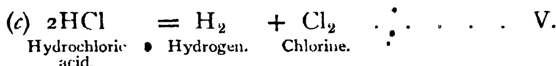
1 : 1·33 : 1·5 : 3



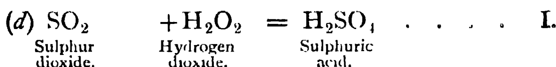
56. (*a*) $Na_2 + 2OH_2 = 2ONaH + H_2$ V.
Sodium. Water. Sodium hydroxide. Hydrogen.



(*b*) $Fe + H_2SO_4 = FeSO_4 + H_2$ IV.
Iron. Sulphuric acid. Ferrous sulphate. Hydrogen.



(*c*) $2HCl = H_2 + Cl_2$ . . . . . . V.
Hydrochloric acid. Hydrogen. Chlorine.

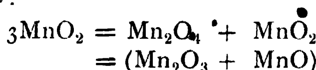


(*d*) $SO_2 + H_2O_2 = H_2SO_4$ . . . . . I.
Sulphur dioxide. Hydrogen dioxide. Sulphuric acid.

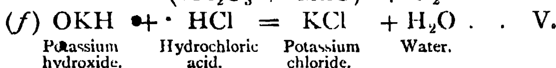


(*e*) $3MnO_2 = Mn_3O_4 + O_2$
Manganese dioxide. Manganous-manganic oxide. Oxygen.

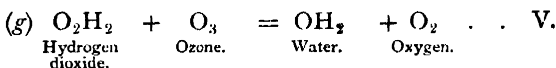
I. and V.



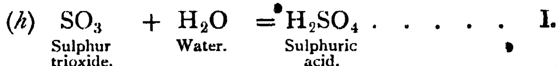
$$3MnO_2 = Mn_2O_4 + MnO_2$$
$$= (Mn_2O_3 + MnO) + O_2$$



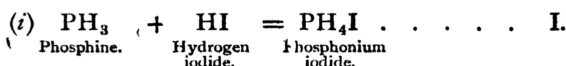
(*f*) $OKH + HCl = KCl + H_2O$ . . V.
Potassium hydroxide. Hydrochloric acid. Potassium chloride. Water.



(*g*) $O_2H_2 + O_3 = OH_2 + O_2$ . . V.
Hydrogen dioxide. Ozone. Water. Oxygen.

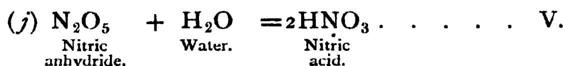


(*h*) $SO_3 + H_2O = H_2SO_4$ . . . . . . I.
Sulphur trioxide. Water. Sulphuric acid.



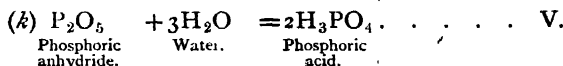
(*i*) $PH_3 + HI = PH_4I$ . . . . . . I.

Phosphine. Hydrogen iodide. Phosphonium iodide.



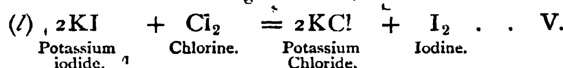
(*j*) $N_2O_5 + H_2O = 2HNO_3$ . . . . . . V.

Nitric anhydride. Water. Nitric acid.



(*k*) $P_2O_5 + 3H_2O = 2H_3PO_4$ . . . . . . V.

Phosphoric anhydride. Water. Phosphoric acid.



(*l*) $2KI + Cl_2 = 2KCl + I_2$ . . . V.

Potassium iodide. Chlorine. Potassium Chloride. Iodine.

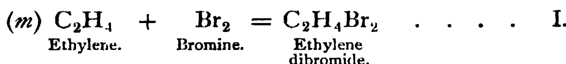
Probably in two stages thus :—



$KI + ClCl = KCl + ICl$ (iodine monochloride)

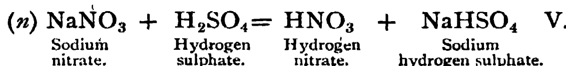


$KI + ICl = KCl + I_2$.



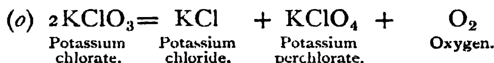
(*m*) $C_2H_4 + Br_2 = C_2H_4Br_2$ . . . . . I.

Ethylene. Bromine. Ethylene dibromide.



(*n*) $NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$ V.

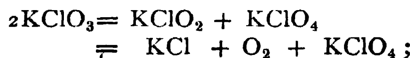
Sodium nitrate. Hydrogen sulphate. Hydrogen nitrate. Sodium hydrogen sulphate.



(*o*) $2KClO_3 = KCl + KClO_4 + O_2$

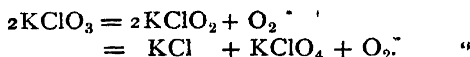
Potassium chlorate. Potassium chloride. Potassium perchlorate. Oxygen.

Probably preceded by a rearrangement :—

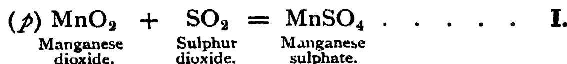


$$2KClO_3 = KClO_2 + KClO_4$$
$$= KCl + O_2 + KClO_4\,;$$

or a kind of double decomposition :—

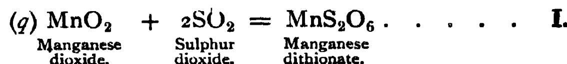


$$2KClO_3 = 2KClO_2 + O_2$$
$$= KCl + KClO_4 + O_2.$$



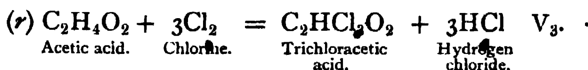
(*p*) $MnO_2 + SO_2 = MnSO_4$ . . . . . . I.

Manganese dioxide. Sulphur dioxide. Manganese sulphate.

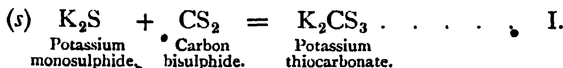


(*q*) $MnO_2 + 2SO_2 = MnS_2O_6$ . . . . . . I.

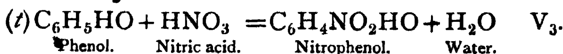
Manganese dioxide. Sulphur dioxide. Manganese dithionate.


(*r*) $C_2H_4O_2 + 3Cl_2 = C_2HCl_3O_2 + 3HCl$ V₃.

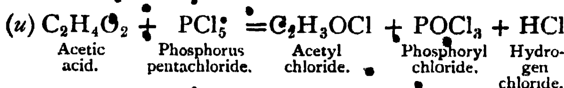
Acetic acid. Chlorine. Trichloracetic acid. Hydrogen chloride.


(*s*) $K_2S + CS_2 = K_2CS_3$ . . . . . . I.

Potassium monosulphide. Carbon bisulphide. Potassium thiocarbonate.


(*t*) $C_6H_5HO + HNO_3 = C_6H_4NO_2HO + H_2O$ V₃.

Phenol. Nitric acid. Nitrophenol. Water.

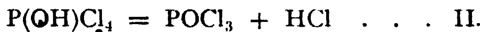

(*u*) $C_2H_4O_2 + PCl_5 = C_2H_3OCl + POCl_3 + HCl$

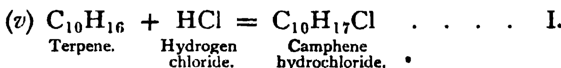
Acetic acid. Phosphorus pentachloride. Acetyl chloride. Phosphoryl chloride. Hydrogen chloride.

Probably preceded by

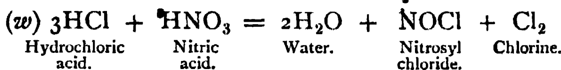

$C_2H_3OOH + PCl_5 = C_2H_3OCl + P(OH)Cl_4$ V.

and

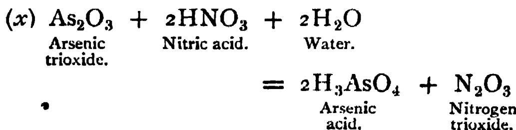

$P(OH)Cl_4 = POCl_3 + HCl$ . . . II.


(*v*) $C_{10}H_{16} + HCl = C_{10}H_{17}Cl$ . . . . . I.

Terpene. Hydrogen chloride. Camphene hydrochloride.


(*w*) $3HCl + HNO_3 = 2H_2O + NOCl + Cl_2$

Hydrochloric acid. Nitric acid. Water. Nitrosyl chloride. Chlorine.

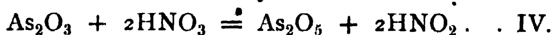

(*x*) $As_2O_3 + 2HNO_3 + 2H_2O$

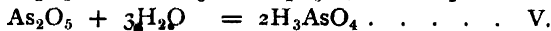
Arsenic trioxide. Nitric acid. Water.

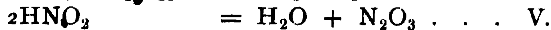
$= 2H_3AsO_4 + N_2O_3$

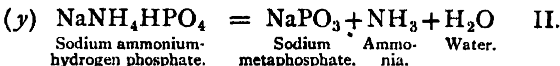
Arsenic acid. Nitrogen trioxide.

Probably preceded by

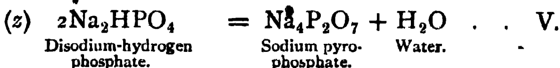

$As_2O_3 + 2HNO_3 = As_2O_5 + 2HNO_2$ . . IV.


$As_2O_5 + 3H_2O = 2H_3AsO_4$ . . . . . . V.


$2HNO_2 = H_2O + N_2O_3$ . . . . V.


(*y*) $NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$ II.

Sodium ammonium-hydrogen phosphate. Sodium metaphosphate. Ammonia. Water.


(*z*) $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$ . . V.

Disodium-hydrogen phosphate. Sodium pyrophosphate. Water.

57. 24182·7 c.c.

58. 2510·47 c.c.

60.

	Atomic weights.	Equivalents.
Mercury . . .	200	100 or 200
Zinc	65·5	32·75
Chlorine . . .	35·5	35·5
Iodine	127	127, rarely $\frac{127}{3}$?
Sulphur . . .	32	$\frac{32}{2}$ or $\frac{32}{4}$ or $\frac{32}{6}$
Iron	56	28 or $\frac{2}{3}$ of 56
Copper. . . .	63·5	31·75 or 63·5

$K_2S = 34$. $PCl_5 = 208·5$.
$AsH_3 = 78$. $H_2SO_4 = 98$.

61. ·4711 gram.

62. ·6220 gram or 6·942 litres.

64. 54·4.

65. From the spec. heat 109·3. The multiple of 56 which falls nearest to this is 112.

66. The atomic weight is 48·75 × 4, whence the spec. heat is $\frac{6·2}{195}$ = ·0317.

70. Empirical formula from the percentages $CH_2O = 30$. 35·5 parts by weight of chlorine replace 1 part by weight of hydrogen, and 100 parts chloracetic acid consist of 37·5 chlorine and 62·5 of acetic acid minus the hydrogen replaced by 37·5 of chlorine. Then

37·5 : 35·5 :: 62·5 : Molecular weight—1.

Ans.—59·16 + 1 = 60·16 or rather 60, and the formula is $C_2H_4O_2$.

72. NaF . Ag_2SO_4 $Hg(CN)_2$. $(Hg_2)_3(PO_4)_2$
$Ba(ClO_3)_2$. $BiCl_3$. Fe_2SiO_4 . $Cu(C_2H_3O_2)_2$
$Fe_2(NO_3)_6$. $Cr_2(C_2O_4)_3$. $Sn_3(PO_4)_4$. $Ca(ClO)_2$

74. At. wt. = $\frac{6·2}{·03}$ = 206·6 (approx.). If 1 part of chlorine combines with 2·915 parts of metal, 35·5 parts

(1 atom) combine with 103·4825. Hence the exact atomic weight is 103·4825 × 2, or 206,965.

75. 108 × ·057 = at. wt. of M × ·0306

Whence M = 201·17.

The nearest multiple of 70 is 210.

Ans. 210 . MCl_3.

76. 179.

77. 322.

78. 328.

79. 215.

80. 213.

81. 119.

82. 154.

83. 96·5.

84. 62.

85. 121.

86. 366.

89. C_2H_6O.

91. C_2H_4O.

92. C_5H_8.

93. $C_{22}H_{24}NO_7$.

94.

Magnetic pyrites	Fe_7S_8
Iron peroxide	Fe_2O_3
Hydrogen peroxide	HO or H_2O_2
Cryolite	Na_3AlF_6
Mannite	$C_3H_7O_3$ or $C_6H_{14}O_6$
Benzoic acid	$C_7H_6O_2$
Caffeine	$C_4H_5N_2O$ or $C_8H_{10}N_4O_2$
Cane sugar	$C_{12}H_{22}O_{11}$
Uric acid	$C_5H_4N_4O_3$

95. $C_{10}H_{15}NO$ and $C_{10}H_{16}NOCl$.

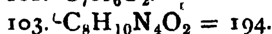
98. $C_7H_4O_2$ or $C_{14}H_8O_4$.

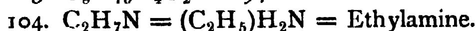
99. $Te_2As_2S_7$.

100. $C_3H_3Cl_3N_2O_2$ or $CH_3(C_2Cl_3O)N_2O$.

101. UCl_5 or U_2Cl_{10}.

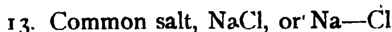

102. $C_7H_6O_2$.


103. $C_8H_{10}N_4O_2 = 194$.

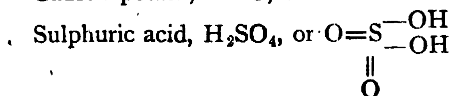

104. $C_2H_7N = (C_2H_5)H_2N$ = Ethylamine.


105. $H_2C_5H_6O_4$ = Pyrotartaric acid.

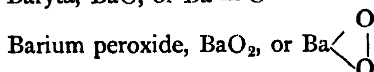
SECTION II.

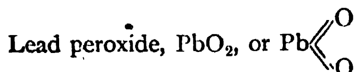

13. Common salt, NaCl, or Na—Cl

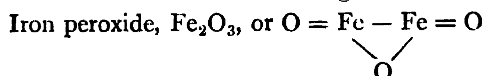

Caustic potash, KHO, or K—O—H

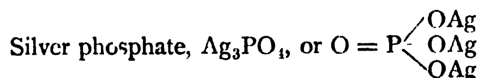

Sulphuric acid, H_2SO_4, or O=S(—OH)(—OH)(=O)

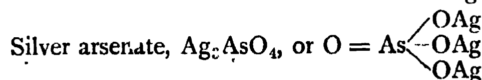

Baryta, BaO, or Ba = O

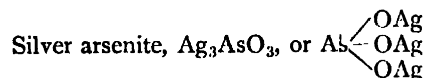

Barium peroxide, BaO_2, or Ba<(O—O)

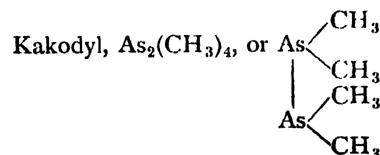

Lead peroxide, PbO_2, or Pb<(=O)(=O)


Iron peroxide, Fe_2O_3, or O = Fe — Fe = O, the two Fe joined through O


Silver phosphate, Ag_3PO_4, or O = P<(OAg)(OAg)(OAg)

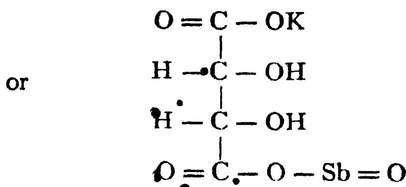

Silver arsenate, Ag_3AsO_4, or O = As<(OAg)(OAg)(OAg)


Silver arsenite, Ag_3AsO_3, or As<(OAg)(OAg)(OAg)


Kakodyl, $As_2(CH_3)_4$, or As<(CH_3)(CH_3) | As<(CH_3)(CH_3)

Tartar emetic, $KSbOC_4H_4O_6OH_2$,

or



23. $3H_2O.SO_3$, or $S(OH)_6$
$3HgO.SO_3$, or $S(O_6Hg''_3)$, Turpeth mineral
$3CuO.SO_3$, or $S(O_6Cu_3)$
$Al_2O_3.SO_3.3H_2O$, or $S(O_6Al_2).3H_2O$, Aluminite.

25. 21·24 pounds.

26. 11·55 grams.

27. 14·59 grams.

29. Sodium 32·86; aluminium 12·86; fluorine 54·28.

30. 43·63 kilos of litharge; 2327·8 litres of oxygen.

31. $AgClO_3$, $AgClO_4$, $AgHSO_4$, Ag_2SO_4, AgH_2PO_4, Ag_2HPO_4, Ag_3PO_4, AgH_3SiO_4, $Ag_2H_2SiO_4$, Ag_3HSiO_4, Ag SiO_4, $AgHSO_3$, Ag_2SO_3, AgH_2PO_3, Ag_2HPO_3.

32.	NO_2Cl	$SO_2.OH.Cl$	$P_2O_3(OH)_3Cl$	C_7H_5OCl
	NO_2NH_2	SO_2Cl_2	$P_2O_3(OH)_2Cl_2$	$C_7H_5ONH_2$
		$SO_2.OH.NH_2$	$P_2O_3(OH)Cl_3$	
		$SO_2(NH_2)_2$	$P_2O_3Cl_4$	
			$P_2O_3(OH)_3NH_2$	
			$P_2O_3(OH)_2(NH_2)_2$	
			$P_2O_3(OH)(NH_2)_3$	
			$P_2O_3(NH_2)_4$	

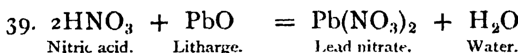
Benzoic acid and carbon acids generally yield also substitution compounds, *e.g.*—

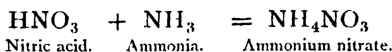
HOC_7H_4ClO Chlorobenzoic acid,
$HOC_7H_3Cl_2O$ Dichlorobenzoic acid,
&c. &c.
$HOC_7H_4(NH_2)O$ Amidobenzoic acid

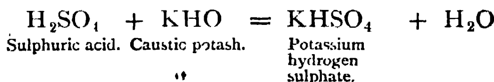
34. $S(OH)_4O = 2H_2O.SO_3$ (glacial sulphuric acid).
$S(OH)_2O_2 = H_2O.SO_3$ (oil of vitriol).
$SO_3 = SO_3$ (sulphur trioxide).
Also $S_2(OH)_2O_5$ (derived from $2S(HO)_6$) $= H_2O.2SO_3$ (Nordhausen acid).

35. Sulphuric	anhydride	SO_3	Known
Phosphoric	„		„
or Pyrophosphoric	„	P_2O_5	„
Nitric	„	N_2O_5	„
Nitrous	„	N_2O_3	„
Hyponitrous	„	N_2O	„
Theiosulphuric	„	S_2O_2	Unknown
Chloric	„	Cl_2O_5	„
Perchloric	„	Cl_2O_7	„
Acetic	„	$(C_2H_3O)_2O$	Known

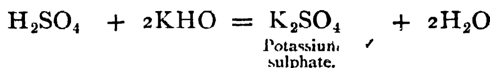
38. Hyposulphites $O{=}S\begin{cases}OM' \\ H\end{cases}$ analogous to hypophosphites and phosphites, &c.

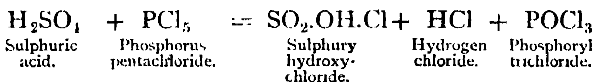
39.

$2HNO_3 + PbO = Pb(NO_3)_2 + H_2O$
Nitric acid. Litharge. Lead nitrate. Water.


$HNO_3 + NH_3 = NH_4NO_3$
Nitric acid. Ammonia. Ammonium nitrate.

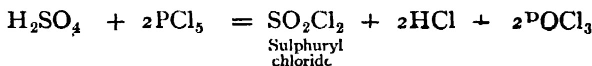

$H_2SO_4 + KHO = KHSO_4 + H_2O$
Sulphuric acid. Caustic potash. Potassium hydrogen sulphate.

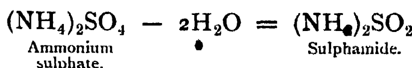
or


$H_2SO_4 + 2KHO = K_2SO_4 + 2H_2O$
Potassium sulphate.


$H_2SO_4 + PCl_5 = SO_2.OH.Cl + HCl + POCl_3$
Sulphuric acid. Phosphorus pentachloride. Sulphury hydroxy-chloride. Hydrogen chloride. Phosphoryl trichloride.

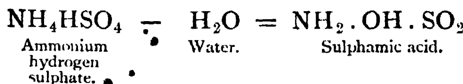
or


$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2HCl + 2POCl_3$
Sulphuryl chloride



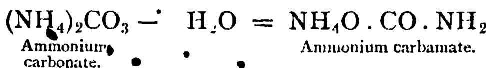
$$(NH_4)_2SO_4 - 2H_2O = (NH_4)_2SO_2$$

Ammonium sulphate. — Sulphamide.



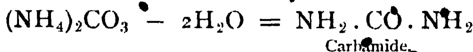
$$NH_4HSO_4 - H_2O = NH_2 . OH . SO_2$$

Ammonium hydrogen sulphate. — Water. — Sulphamic acid.



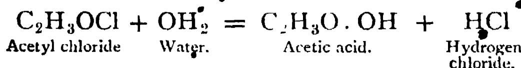
$$(NH_4)_2CO_3 - H_2O = NH_4O . CO . NH_2$$

Ammonium carbonate. — Ammonium carbamate.



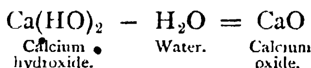
$$(NH_4)_2CO_3 - 2H_2O = NH_2 . CO . NH_2$$

Carbamide.



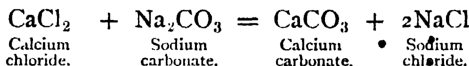
$$C_2H_3OCl + OH_2 = C_2H_3O . OH + HCl$$

Acetyl chloride — Water. — Acetic acid. — Hydrogen chloride.



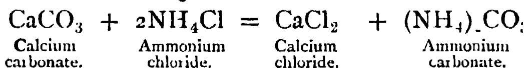
$$Ca(HO)_2 - H_2O = CaO$$

Calcium hydroxide. — Water. — Calcium oxide.



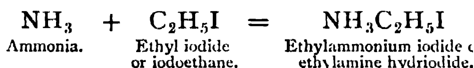
$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Calcium chloride. — Sodium carbonate. — Calcium carbonate. — Sodium chloride.



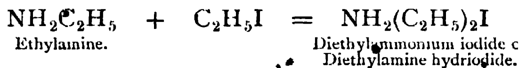
$$CaCO_3 + 2NH_4Cl = CaCl_2 + (NH_4)_2CO_3$$

Calcium carbonate. — Ammonium chloride. — Calcium chloride. — Ammonium carbonate.



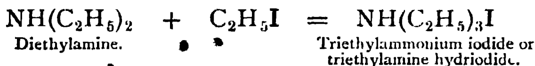
$$NH_3 + C_2H_5I = NH_3C_2H_5I$$

Ammonia. — Ethyl iodide or iodoethane. — Ethylammonium iodide or ethylamine hydriodide.



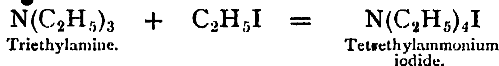
$$NH_2C_2H_5 + C_2H_5I = NH_2(C_2H_5)_2I$$

Ethylamine. — Diethylammonium iodide or Diethylamine hydriodide.



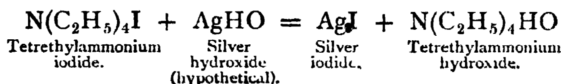
$$NH(C_2H_5)_2 + C_2H_5I = NH(C_2H_5)_3I$$

Diethylamine. — Triethylammonium iodide or triethylamine hydriodide.



$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

Triethylamine. — Tetrethylammonium iodide.



$$N(C_2H_5)_4I + AgHO = AgI + N(C_2H_5)_4HO$$

Tetrethylammonium iodide. — Silver hydroxide (hypothetical). — Silver iodide. — Tetrethylammonium hydroxide.

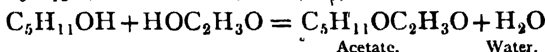
46. 43·75 litres.

47. C 36·6, H 2·1, Ag 47·1, O 13·9.

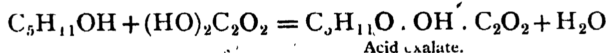
·2705 gram of silver.

50. $C_2H_2O_4$.

54. $C_5H_{12}O$, if an alcohol, is $C_5H_{11}OH$.

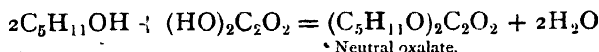


$$C_5H_{11}OH + HOC_2H_3O = \underset{\text{Acetate.}}{C_5H_{11}OC_2H_3O} + \underset{\text{Water.}}{H_2O}$$



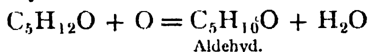
$$C_5H_{11}OH + (HO)_2C_2O_2 = \underset{\text{Acid oxalate.}}{C_5H_{11}O \cdot OH \cdot C_2O_2} + H_2O$$

or



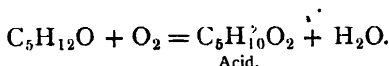
$$2C_5H_{11}OH + (HO)_2C_2O_2 = \underset{\text{Neutral oxalate.}}{(C_5H_{11}O)_2C_2O_2} + 2H_2O$$

If a primary alcohol :—



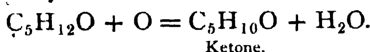
$$C_5H_{12}O + O = \underset{\text{Aldehyd.}}{C_5H_{10}O} + H_2O$$

and



$$C_5H_{12}O + O_2 = \underset{\text{Acid.}}{C_5H_{10}O_2} + H_2O.$$

If a secondary alcohol :—



$$C_5H_{12}O + O = \underset{\text{Ketone.}}{C_5H_{10}O} + H_2O.$$

If a tertiary alcohol, oxidation yields a mixture of acids or of ketone and acid.

55. Aldehyds.

(*a*) $COH - CH_2 - CH_2 - CH_3$.

(*b*) $COH - CH = (CH_3)_2$.

Ketone $CH_3 - CO - C_2H_5$.

56. Dihydric alcohol, $C_7H_{12}(OH)_2$

Monobasic acid, $C_6H_{13}(COOH)$

Compound ether, $CH_3C_6H_{11}O_2$

or $C_2H_5C_5H_9O_2$

&c. &c.

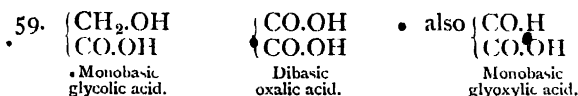
or $C_6H_{13}CHO_2$.

58. Alcohol, $C_nH_{2n+1}OH$

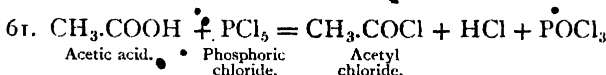
Acetate, $C_nH_{2n+1}O.C_2H_3O$

Aldehyd, $C_nH_{2n-1}.CO.H$

Acid, $C_nH_{2n-1}CO.OH$.

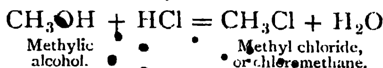


59. $\begin{cases} CH_2.OH \\ CO.OH \end{cases}$ Monobasic glycolic acid. $\begin{cases} CO.OH \\ CO.OH \end{cases}$ Dibasic oxalic acid. also $\begin{cases} CO.H \\ CO.OH \end{cases}$ Monobasic glyoxylic acid.



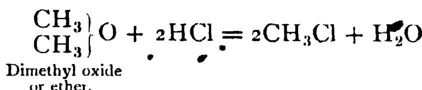
61. $CH_3.COOH + PCl_5 = CH_3.COCl + HCl + POCl_3$

Acetic acid. Phosphoric chloride. Acetyl chloride.



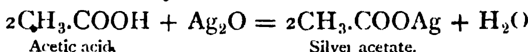
$CH_3OH + HCl = CH_3Cl + H_2O$

Methylic alcohol. Methyl chloride, or chloromethane.



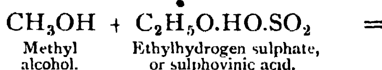
$\left.\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right\} O + 2HCl = 2CH_3Cl + H_2O$

Dimethyl oxide or ether.



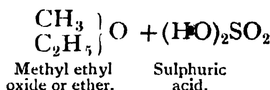
$2CH_3.COOH + Ag_2O = 2CH_3.COOAg + H_2O$

Acetic acid. Silver acetate.



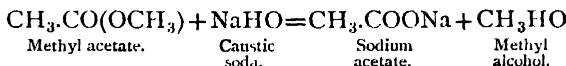
$CH_3OH + C_2H_5O.HO.SO_2 =$

Methyl alcohol. Ethylhydrogen sulphate, or sulphovinic acid.



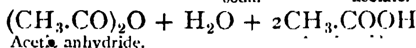
$\left.\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\right\} O + (HO)_2SO_2$

Methyl ethyl oxide or ether. Sulphuric acid.



$CH_3.CO(OCH_3) + NaHO = CH_3.COONa + CH_3HO$

Methyl acetate. Caustic soda. Sodium acetate. Methyl alcohol.

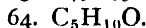


$(CH_3.CO)_2O + H_2O + 2CH_3.COOH$

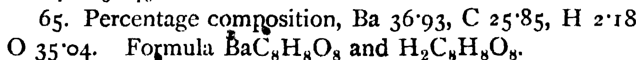
Acetic anhydride.



63. $C_{10}H_{18}O_3$.



64. $C_5H_{10}O$.



65. Percentage composition, Ba 36·93, C 25·85, H 2·18 O 35·04. Formula $BaC_8H_8O_8$ and $H_2C_8H_8O_8$.



66. $HC_9H_{10}O_2$.

SECTION III.

1. ·4141 c.c.

2. (*a*) 1·2705 c.c.

(*b*) Nitrogen 65·28, oxygen 34·72 per cent.

3. 1239·8 c.c.

4. 39107 c.c., or 39·107 litres.

5. Neglecting the change in the relative pressures of the two gases consequent upon their unequal solubility. Oxygen 24·61, nitrogen 75·39 per cent.

Or, correctly as follows—

There are 4 volumes of water, 1 volume of oxygen, and 3 volumes nitrogen.

Let the residual oxygen after absorption be $1-x$.

Residual nitrogen $3-y$.

The oxygen forms $\frac{1-x}{4-x-y}$ of the whole, and is therefore at that pressure.

The oxygen dissolved is therefore

$$4 \times \cdot 04114 \times \frac{1-x}{4-x-y} = x \quad . \quad . \quad . \quad \text{I}$$

Similarly the nitrogen dissolved is

$$4 \times \cdot 02035 \times \frac{3-y}{4-x-y} = y \quad . \quad . \quad . \quad \text{II.}$$

Let $4 \times \cdot 04114 = a$; $4 \times \cdot 02035 = b$.

Then multiply I. by b and II. by a, and add together

$$\text{whence } x = \frac{a}{b}(b-y).$$

Substitute this in Equation II.

$$\frac{(3-y)\,b}{4-y-\frac{a}{b}(b-y)} = y$$

$$(b-a)y^2 - (b^2 + 4b - ab)\,y = -3b^2$$

$$-\cdot 07236\,y^2 - (\cdot 0085 + \cdot 3688 - \cdot 01517)\,y = -\cdot 0255$$

$$\cdot 07236\,y^2 + \cdot 36213\,y = \cdot 0255.$$

Divide by ·07236.

$$y^2 + 5{\cdot}00456\,y = {\cdot}3524$$

$$y^2 + 5{\cdot}00456\,y + 2{\cdot}5023^2 = {\cdot}3524 + 2{\cdot}5023^2$$

$$\therefore\ y = {\cdot}0694.$$

Substitute this value of y in Equation II.

and $$x = {\cdot}03717.$$

Whence the residual oxygen is $1 - {\cdot}03717$.

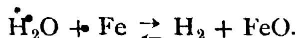
„ „ nitrogen is $3 - {\cdot}0694$.

Oxygen = ·96283, or 24·73 per cent

Nitrogen = 2·9306, or 75·27 „

This is the composition of the residual air.

9. The reaction may be expressed as follows :—



$$H_2O + Fe \rightleftarrows H_2 + FeO.$$

The active masses of the hydrogen and steam are proportional to their respective pressures, and the ratio of the pressures is constant or

$$\frac{46}{258} = \frac{101}{579} \text{ nearly.}$$

10. H + Cl + water = 39320 calories.

$Zn\frac{1}{2}$ + Cl + water = $\frac{112840}{2}$ = 56420.

or 2(H + Cl + water) = 39320 × 2 = 78640.

and Zn + Cl_2 + water = 112840.

Hence zinc decomposes aqueous hydrochloric acid.

Order :

(1) Zinc, (2) Cadmium — decompose dilute hydrochloric acid.

(3) Copper, (4) Mercury, (5) Gold — do not decompose dilute hydrochloric acid.

11. {Caustic potash . 56 parts.
{Iodine . . . 127 „
{Copper . . . 31·75 „
{Oxygen . . . 8 „
{Sulphuric acid . 49 „
{Hydrogen . . 1 „
{Chlorine . . 35·5 „
{Hydrogen . . 1 „
{Oxygen . . . 8 „

12. Two atoms of copper and two atoms of chlorine. One atom of zinc is dissolved in each cell.

13. 8080 grams.

14. 1456·6 grams.

15. $\frac{5747}{2 \cdot 29s + 4 \cdot 32 \times \cdot 2438}$.

If the specific heat, *s*, of phosphoric anhydride is taken as ·2, the answer is 3803°.

16. In estimating the 'heat of combustion' of hydrogen, the heat communicated to the calorimeter includes the heat resulting from the liquefaction of the steam, and from cooling the resulting water from 100° to 0°.

$$\frac{34034 - [(537 + 100)9]}{(9 \times \cdot 475) + (26 \cdot 7 \times \cdot 2438)} = 2625°.$$

17. 16372 kilos.

18. 117·9 grams.

19. 100 litres of the gas produce heat enough to raise the temperature of 127,878 grams, or 127·878 kilograms of water 1°. The heat required is 2000 × (100 + 537) = 1,274,000 kilo-units. The volume of gas requisite is therefore 996,245 litres.

20. 143·7 and 287·4.

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